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TESTED METHODS OF MINERAL ANALYSIS

By

B. T. KITTO

With a Foreword by

BENEDICT KITTO, F.I.C., F.G.S., HON.M.I.M.M

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FOREWORD

THE Author in this little book has set out in plain language and minute detail methods of assaying various ores—especially of some of the rarer metals—which, after hundreds of tests and researches, in which he has had twenty years experience in my Assay Office and Laboratory, have been found to give accurate results

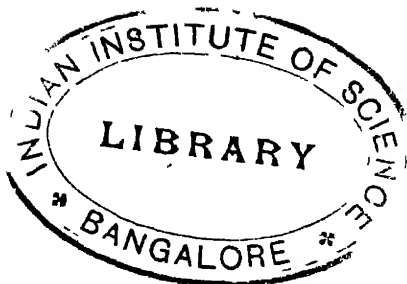
In the hands of anyone with ordinary manipulative ability the methods given in such detail can be depended upon. I need scarcely add that the work is published with my consent.

BENEDICT KITTO,

F I C , F G S , Hon M I M M

366 CITY ROAD,

LONDON, E C 1



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PART I

THE BASIC MANIPULATIONS OF ORE ANALYSIS

IN order to arrive at the correct commercial value of a parcel of ore running sometimes into thousands of tons in weight, and to guide the metallurgist in his treatment of it to extract the "values" it contains, a sample is submitted for examination to a chemist. It is essential, then, that this sample shall represent exactly the parcel from which it is drawn. Unless it does, the results of an analysis, whether for one, two or more elements, or a complete analysis, will be of little value, an incorrect price will be paid and received for it, the metallurgist will fail to recover as much as the sample indicates should be recovered, or he may get more, he may even spoil the whole parcel by wrong treatment. To the sampling then, much care and common sense is to be applied.

The ore may be presented to the sampler loose, in truck or wagon-loads, it may be in a pile, or bagged in lots of a hundredweight or two. It may be in large lumps, each weighing many pounds, or quite fine, or mixtures of coarse and fine. Upon the condition of the ore the sampler has to decide upon the method of sampling it.

Suppose the ore is bagged, and proves on inspection to be fine (passing a 20 or 30 mesh sieve) it will not be necessary to turn it out, but a sample may be obtained by the use of the "sampling-iron." This instrument is essentially a narrow semicircular scoop of iron. Its length may vary from 18 inches to 30 inches, it is about an inch wide, half an inch deep, and divided at half its length by a bar of iron. It has a wooden handle like a shovel. The iron is thrust down through the middle of the opened bags, and the ore thus withdrawn thrown into a heap. This heap is mixed by two or more men standing equidistant from each other, and shovelling the ore regularly into another pile, each shovelful being thrown on the top of the last, and the last of the ore brushed up and thrown on the top. This operation is repeated until the ore is deemed to be mixed, when the final pile is flattened down, the flattening process being begun at the top, and performed regularly around the pile to the outside, until a round flat mass of ore is obtained. This is then quartered by drawing with a shovel two transverse diameters. Two opposite quarters are removed completely, to the sweeping up of the fine dust. The remaining quarters are mixed by throwing alternate shovelfuls from each into a new heap, and the mixing and quartering process continued until a sample is obtained of some 4 to 5 pounds, which is carried to the assay office for preparation for the chemist.

In mixing parcels of lumpy ore for sampling, the proportion of the size of the lumps to that of the whole bulk should be noted. In the case of a 5-ton pile, for instance, the ore must be crushed till it is reduced to lumps equal to not more than 4-inch cubes in size,

when this is quartered, then the lumps must be reduced to half that size before efficient mixing can be done, and so on till the final sample is reached, which should pass a sieve of 20 holes to the linear inch.

When ore is being sampled, a "moisture sample" is drawn, and kept in an accurately corked and sealed—or better—stoppered bottle. This can conveniently be done by taking dips regularly over the pile, when it will pass, say a 10 mesh sieve, of about two ounces at a time, dipping to the bottom of the mass with a small flour scoop, or similar article, until some two pounds is collected. In the case of ores of the precious metals, where the yield of values is usually so small as to be returned as ounces, etc., per ton of ore, where the ore is apparently dry, this moisture sampling, of course, is not done.

When the ore is distinctly wet, as in the case of dressed or concentrated ore very often, it will be fine enough at the start to extract the moisture sample, and it should be done at this stage. If it is in casks or drums the sampling iron may be used, the pile quickly mixed, flattened down, and a sample quickly drawn with the flour scoop.

Moisture determinations are best done on a medium fine balance in a counterpoised porcelain dish of 4–5 inches diameter, on 100 grams. This is dried in a water oven at 100° C, being occasionally gently stirred with a short glass rod. The drying is continued till no condensation takes place on a cold clock-glass which is placed over the dish. When small samples are being dealt with the determination is done on 10 grams on a fine balance, a crucible of convenient size being used. Unless the results of analysis are especially asked for

“on sample taken or received,” they are returned “on sample dried at 100° C” The method of returning the result should be stated in the assay book on every sample examined The chemist’s portion, ground to pass an 80 or 90 mesh sieve, will be dried with the same precautions as the moisture determination, and if the results are to be returned “on sample taken or received” the figures are calculated to the wet sample For example Say the result of the assay of a Tin ore gave 15.75% of Tin, and the determination of moisture showed 0.15%, then the content of Tin on the sample as taken or received is $15.75 \times \frac{100 - 0.15}{100} = 15.73\% \text{ Tin}$

Or again, a dressed Wolfram gave 70.30% WO_3 , moisture, 1.45% Then $70.30 \times \frac{100 - 1.45}{100} = 69.28\% \text{ WO}_3$

Minerals containing elements in the metallic state often cannot be crushed completely to pass the meshes of the sieves The metallics remain on the sieve after the crushable portion of the sample has passed through If these appear on the 20 mesh sieve it is best to put the whole through the 90 The metallics are carefully collected and weighed The crushed portion is also weighed Suppose the crushable portion of a sample of copper ore weighed 151.4 grams and the metallics 0.27 grams Then the total weight of ore concerned is 151.67 grams Now suppose a gram is to be taken for assay, then of the fine portion $\frac{151.4}{151.67}$ of a gram is taken, or 0.9982 gram, and $1 - 0.9982$ gram of metallics = 0.0018 gram Now to get this correctly it will be necessary to dissolve up the metallics in acid, say aqua regia, make the solution up to a definite volume with water,

and take a part representing the amount required. Thus, suppose the 0.27 gram in solution is made up to 30 ccm, then 0.0018 being 0.6667% of 0.27 gram the amount required is 0.6667% of 30 ccm or 0.20 ccm. The ore is weighed into the vessel to be used, and 0.2 ccm of the "metallics" solution is run into it from a burette, and the assay proceeded with in the usual way. Where round prills of metal are met with, these may be flattened on a clean anvil to render solution more rapid.

It will help the chemist considerably, on being presented with an ore for analysis, to examine it on a "pan." This is a slightly concave disc of iron, some 10 to 12 inches in diameter. The minerals show up well if the pan is enamelled white. Some 5-10 grams of the sample are thrown on the pan. Water is run on to it until it is well covered, the whole is thoroughly wetted, if necessary by stirring it with the finger, and if some floats, it is flicked down with water from the fingers. The pan is given a rapid circular motion till the whole mass is moving, and then allowed to settle for a few seconds, most of the water is run off, enough is left to enable the whole of the wet ore to be brought into the middle. The pan is then given a succession of rapid little jerks, being held in a slightly slanting position, and the jerks made in an upward direction in such a way as to throw up the heavier minerals from under the lighter ones. After a few jerks, the water is gently passed over the ore, washing away the light siliceous matter from the heavier minerals. A skilful panner will separate nearly all the "gangue" in this way, note the proportion, and wash the whole off the pan. The minerals remaining may be examined

in a similar way where the specific gravities differ sufficiently. By this method the chemist is quickly familiarized with the material under examination, and is guided in the amount of ore to take for his tests, and what impurities are especially to be removed.

Some ores are so refractory as to cut up very badly the ordinary cast iron mortars. In these cases mortars of chilled steel should be used and a magnet passed over the ore to remove any particles of iron introduced from the pestle and mortar, and the sample reduced to an impalpable powder in an agate mortar.

In helping to identify minerals, especially those much alike in appearance, but of different chemical composition, the determination of the specific gravity is helpful. When using a specific gravity bottle, the sample is crushed just fine enough to pass into it. Wash out the bottle, rinse out with distilled water, and dry in an oven, quickening the process by pumping into it at intervals air from a blowpipe. Allow to cool, and weigh. Pass into it about 10 grams of the sample, and weigh again. Now fill almost to the neck with cold boiled distilled water at 59° to $59\frac{1}{2}^{\circ}$ F., tap the bottle vigorously to dislodge air bubbles clinging to the lumps, fill up with water, replace the stopper, wipe the outside quite dry with a clean towel, and weigh quickly. It will be found on testing the temperature that it is just 60° in most cases. The temperature should be adjusted to 60° F., and another weighing done, if it is not at that temperature. The weight of the bottle filled with water at 60° F. must be determined. Get the sum of the weight of sample taken and of the bottle filled with water. Subtract from this the weight of the bottle containing the sample and

. . .

water The result shows the weight of water displaced by the sample Then the weight of the sample taken, divided by the weight of water displaced, gives the specific gravity of the sample

In the following procedures of mineral analysis, distilled water is always used, and all open vessels covered during boiling with watch—or clock—glass, and fusions with appropriate covers, porcelain or silica vessels with porcelain lids, platinum ones with platinum lids, and so on

PART II

ALUMINIUM

THE ores of Aluminium provide some of the hardest of minerals, the chief being Corundum, oxide of Aluminium, Corundum (Sapphire) $H = 9$, $G = 3.9-4.1$, $Stk =$ light grey, and Emery, the oxide, with iron oxide. Bauxite is a hydrated oxide, while the clays, notably china clay, contain Aluminium in conjunction with silica, etc.

In the case of the very refractory minerals of Aluminium as Corundum and Emery, it is best to reduce the sample to the utmost possible fineness in a steel mortar. The final sample must be gone over with a magnet to extract metallic particles of iron worn from the pestle and mortar.

Procedure A

In the case of rich samples of Corundum and Emery, which are only slightly attacked by acid, the sample is ground as above, and 0.2-0.3 gram weighed into a platinum crucible, with 3 grams of a mixture of about equal parts of Na_2CO_3 and K_2CO_3 . The whole is mixed in the crucible with a stout platinum wire, and heated, gently at first, over a Bunsen, with

crucible covered with a platinum lid. The heat is increased until the mass fuses, and is finally blow-piped, the molten mass being occasionally gently rotated, and the heating continued till fusion is seen to be complete. It is allowed to become quite cold, and is then placed in a 250 c c beaker, and covered with boiling water, and the lid is washed in. It is allowed gently to simmer in the covered beaker until the mass is dissolved away from the crucible, or it may be removed therefrom by gentle pressure with a clean glass rod. Wash out the crucible thoroughly into the beaker, and add pure HCl cautiously until the solution no longer effervesces, and then 5-10 c c. in excess. The volume of liquid is reduced by boiling down to about 60 or 70 c c and is transferred and washed into a porcelain dish of some 150 c c capacity. If any specks of undecomposed mineral are observed at this point, the solution must be filtered into the dish through a 9 cm fine paper, and washed, dried and ignited, and re-fused with a gram or two of the fusing mixture, and treated in the same way, and added to the original solution. This solution is evaporated completely on the water bath, then given an hour in the water oven, or till no pungent acid can be smelt. It is taken up with 15 c c pure HCl, again evaporated, finishing in the oven as before. It is again taken up with 15 c c pure HCl, brought carefully to the boil, and 20 c c boiling distilled water added, and stirred well with a glass rod. The silica is filtered off through a 9 cm or 12½ cm fine paper and washed thoroughly with hot water into a 300 c c conical flask. A stream of H_2S is passed through the hot assay to remove any group 2 metals.

The sulphides, if any, are filtered off and washed well. The filtrate is boiled free from H_2S . Add to the assay 20 c.c. cold saturated solution of ammonium phosphate, then add dilute NH_4HO till a faint turbidity persists. Just clear the solution with only as much dilute pure HCl as is necessary and add 10 grams solid $\text{Na}_2\text{S}_2\text{O}_3$. Bring to the boil, and while boiling add 20 c.c. 30% acetic acid. Boil for seven minutes and filter on a $12\frac{1}{2}$ cm fine paper. Wash thoroughly until free from chlorides with a drop or two of 3% solution of ammonium phosphate in hot water. Dry and ignite in a silica or porcelain crucible, gently at first, and finally to a bright redness. When cold weigh as AlPO_4 . Factor for $\text{Al}=0.2219$. Log of factor $\overline{1}34616$. It is best to treat the ppt again by transferring to a small beaker, crushing the lumps carefully with a glass rod, and washing again with the wash solution, dry and ignite again.

Procedure B

In the presence of Chromium or Uranium fuse the agated ore with ten times its weight of pure fused KHSO_4 in a silica crucible, keeping it covered, and heating gently at first till water is driven off, and raising the heat to redness, rotating the crucible gently now and then to include all the mineral in the molten mass. Continue at red heat for five minutes. Allow to cool completely and extract the melt with hot water into a 400 c.c. beaker flask and wash out the crucible and lid. Add 10 c.c. dilute H_2SO_4 and boil till nothing remains but insoluble silica. Filter this off through a 9 cm fine paper into a 750 c.c. conical flask and

wash well with hot water To the warm filtrate add $\frac{N}{10}$ $K_2Mn_2O_8$ till a faint pink colour persists, and add cautiously dilute NH_4HO in slight excess, and 3 grams $(NH_4)_2CO_3$ Bring to the boil, allow to settle, and filter off through a $12\frac{1}{2}$ or 15 cm fine paper Wash with hot water till free from sulphates, and wash back the ppt into the conical flask and dissolve in sufficient pure dilute HCl Now proceed as in Procedure A, adding the ammonium phosphate solution, and proceeding as there described

Procedure C

In the case of small quantities of Al, it may be determined as described in an example of the complete analysis of Wolfram, page 115

Procedure D

Another method for determining small quantities of Al depends on the solubility of its hydrate in solution of KHO The iron and alumina are brought down as in "Wolfram" analysis finally as hydrates with NH_4HO , these are dissolved in pure dilute HCl , and the solution poured into a solution of KHO in a silver dish, the KHO being sufficient to give an excess when the acid solution of hydrates is poured into it. The solution is warmed up, and filtered through a $12\frac{1}{2}$ cm. fine paper, having been diluted with water to prevent the strong caustic alkali from destroying the paper Filter into a 750 c c conical flask containing 100 c.c cold water The ppt is dissolved in HCl , and retreated with KHO , and the filtrates combined, the iron ppt washed with hot water The filtrate is

rendered acid with dilute HNO_3 , and dilute HCl added to clear it, if necessary, and the Al brought down with a small excess of dilute NH_4HO . This is nearly all boiled off, the ppt allowed to settle and filtered through a $12\frac{1}{2}$ cm fine paper, and washed by decantation with a hot 5% slightly ammoniacal solution of NH_4NO_3 six times, then on the paper, where it is washed free from soluble salts. Dry and ignite, finally strongly in a weighed platinum crucible, and weigh when cold. Ignite again strongly and weigh again. Take the constant weight. The compound is Al_2O_3 . Factor for Al is 5294. Log of factor 1.72379.

ANTIMONY

The chief ore of this metal is the sulphide, Stibnite or Antimonite. It has a streak of lead-grey colour. Specific gravity 4.5 to 4.6 and hardness 2. There are also Jamesonite, a sulphide of Lead and Antimony, and other sulphides.

Procedure A

In cases of good samples of Stibnite, weigh 0.4 gram of the sample into a 300 c c conical flask and add 30 c c of pure HCl . Place a small stemless funnel in the neck of the flask, and warm the assay till all the H_2S is evolved. Now cautiously add about 2 c c bromine drop by drop, and place on a warm part, gradually warming up till most of the bromine is removed. The fumes may be frequently blown out with a glass tube. Now add in crystals 0.75 gram of sodium sulphite,

rotating the assay gently till the sulphite is dissolved. Now boil the assay (the funnel still in the flask) until a third of its bulk is evaporated. This serves to remove the excess of SO_2 evolved from the sulphite, which reduces the antimonious chloride to antimonous chloride. Wash in the funnel with 10 c c boiled distilled water, add 10 c c further pure HCl , bring the assay to the boil and titrate immediately with a standard solution of potassium bromate, using a drop of methyl orange as indicator, the end point is indicated by the discharge of the pink colour, giving place to a pale straw colour. A standard solution of potassium bromate is prepared by dissolving 2.82 grams of the pure salt in distilled water, and diluting to one litre. It is sometimes possible to obtain practically pure metallic Antimony which may be used as a standard. Its purity should be determined by analysis. A more reliable substance for standards is antimony potassium tartrate, obtainable in a very pure form, which may, if necessary, be recrystallized from aqueous solution. Potassium antimony tartarate, $\text{C}_4\text{H}_4\text{KSbO}_7$, contains 37.015% of Antimony. For a standard take 1.0807 grams of the salt (=0.4 gram Sb) and proceed in the same manner as the assay of the rich samples. To obtain the best results a standard is run with each determination on (as nearly as possible) the same amount of Antimony as is contained in the sample for assay.

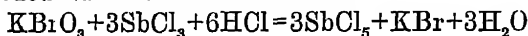
Procedure B

In the case of samples poor in Antimony, it becomes necessary first to separate it as sulphide, and then proceed as in Procedure A.

From 3 to 5 grams of the sample is weighed into a

250 c c beaker flask, treated with 15 c c pure HNO_3 , and brought gradually to dryness on the hot-plate. When cold 20 c c pure HCl are added and boiled down to two-thirds the bulk. Add an equal bulk of hot distilled water, allow to settle, and filter off through a 9 cm or $12\frac{1}{2}$ cm fine paper into a 500 c c conical flask, and wash well with hot water, to each wash add 2 c c pure HCl to keep up the antimony chloride. Dilute the assay to about 300–400 c c with hot water, and pass a rapid stream of H_2S into the boiling solution, shaking the flask around to facilitate precipitation of the sulphides. When saturated, shake thoroughly and allow to settle completely on a warm part. Filter rapidly through a $12\frac{1}{2}$ cm fine paper, and wash with hot H_2S water containing a few drops of pure HCl , about four times. Wash the sulphides back into the conical flask without opening the paper, place the funnel with the paper in another 500 c c conical flask. Treat the sulphides with 10 c c of a saturated solution of potassium sulphide, bring to the boil, settle and filter off through the same paper. The antimony sulphide is now in solution. Wash well with hot water containing about 10% of the K_2S solution. The solution containing antimony is brought to a temperature of about 90°C , a moderate excess of pure HCl is added without shaking, and the assay allowed to stand for twenty minutes on a warm part. It is now thoroughly shaken, gently at first, to avoid a rush of gas, but finally very thoroughly. If the assay does not smell strongly of H_2S , a stream of the gas is passed into it for five to ten minutes. It is allowed to settle, and filtered off through a $12\frac{1}{2}$ cm fine paper (or 9 cm for small amounts), and washed once with hot H_2S water. It is

then washed into a 300 c c conical flask with 30 c c strong HCl, the opened paper being given a final wash with 10 c c hot water. The flask is covered with a small stemless funnel, and gently warmed till most of the orange sulphide is dissolved. Two c c of bromine are slowly added to the cooled assay, and the estimation proceeded with as in Procedure A.



ARSENIC

The chief ore of Arsenic is Mispickel, or Aisenical Pyrites. It has a specific gravity of 5.9-6.2, hardness 5.5-6, and streak greenish black.

Procedure A

In good samples of pyrites place 0.5 gram in a 250 c c beaker flask, add cautiously 10 c c pure HNO₃. When spontaneous action ceases boil down gradually to dryness till no acid can be smelt at the mouth of the beaker. Next add 0.4 gram of Na₂SO₃ and 20 c c hot water and boil for five minutes. Add slowly 20 c c of 4-1 dilute H₂SO₄ and boil the assay until SO₂ can no longer be smelt in the steam. Bring the bulk to some 50 c c. with hot water, and pass a rapid stream of H₂S into it until the yellow sulphide of Arsenic is being freely precipitated. Then add 1-1NH₄HO until the acid is neutralized and the assay turns black from precipitation of iron sulphide, add a further 10 c c of the NH₄HO and continue to digest with H₂S for half an hour. At the end of this time the assay will be

found on settling to have assumed a yellow-coloured solution. Remove from H_2S , bring just to the boil carefully avoiding bumping and allow to settle completely. Filter off through a $12\frac{1}{2}$ cm fine paper into a 750 c c conical flask, and wash three times with hot water, at each wash adding a c.c. or two of $(\text{NH}_4)_2\text{S}$ solution. Next wash back the ppt by opening the paper. Pour over the paper enough pure HCl to dissolve the black sulphides and wash paper well and warm up, but do not boil the assay. Pass H_2S and add a slight excess of dilute NH_4HO . Pass the gas for some ten minutes, bring to the boil, settle, filter and wash well with hot water and $(\text{NH}_4)_2\text{S}$. The combined filtrates are nearly neutralized with pure HCl , and allowed to stand on a warm spot for 15 minutes. Then acidify carefully and add 5 c c. in excess of pure HCl . Shake the assay vigorously (beginning cautiously in case there is a violent evolution of gas), and allow to stand overnight, wrapping a filter paper around the mouth of the flask. The assay should smell strongly of H_2S , if it does not do so a further stream must be passed through. Filter the precipitated sulphide through a $12\frac{1}{2}$ cm fine paper, and wash with warm water, slightly acidified with H_2SO_4 and containing H_2S , until the filtrate gives no reaction for chlorides. Wash the ppt back into the flask from the opened paper, and pour over it 10 c c of warmed pure HNO_3 . Wash the paper thoroughly into the flask and boil down till the separated sulphur runs into globules, and most of the HNO_3 is evaporated. Shake the flask to break up the globules and rinse down the sides of the flask with 20 c c. cold water. Place in the solution a piece of litmus paper, and render the assay *just* alkaline with

dilute NH_4HO (One NH_4HO to two H_2O) Then add 5 c c. of dilute acetic acid (1-1) and 0.5 gram of sodium acetate (A stock solution of 100 grams of acetate, 500 c c acetic acid, made up to a litre with water is kept) Bring the bulk to some 200 c c and titrate boiling with a standard solution of uranium acetate, a solution of potassium ferrocyanide being used as indicator in the spotting dish The titration is best performed by abstracting from the assay about 10 c c into a small beaker and titrating the remainder until no more ppt can be seen to be forming, when it is tested, and if a distinct brown colour is formed on the plate, the abstracted portion is added and washed in and the titration continued two or three drops at a time, boiling between each solution until the coloration begins to appear again This indicates the end of the titration To make the standard solution of uranium acetate, dissolve 34 grams of it in water and acetic acid Weigh the salt into a 400 c c conical flask, and add 100 c c distilled water and 5 c c acetic acid (B P) and warm up to about 90°C If the solution is cloudy from small impurities in the salt, filter it into the 1000 c c graduated flask, and repeat the 100 c c of water, and 5 c c acetic acid, using in all 25 c c of the acid, and making the cold solution up finally to a litre Standardize this solution with pure white arsenic, As_2O_3 Dissolve as much in a 750 c c conical flask in 10 c c pure HNO_3 as will contain about as much arsenic as the assay As_2O_3 contains 75.76% Arsenic. The strength of the standard solution is approximately such that each c c equals 0.005 gram of arsenic So that, suppose your 5 gram assay required 32.5 c c, the assay will contain about 0.1625 gram of arsenic. This

is equal to 0.2145 As_2O_3 . Take 0.2 gram (equals 0.1515 gram As). Proceed in an exactly similar manner as in the assay, from the solution of the arsenic sulphide till the sulphur runs into globules, and most of HNO_3 is evaporated, with the exception that, as the approximate number of c.c. required for the standard is known, no solution is abstracted to be added after.

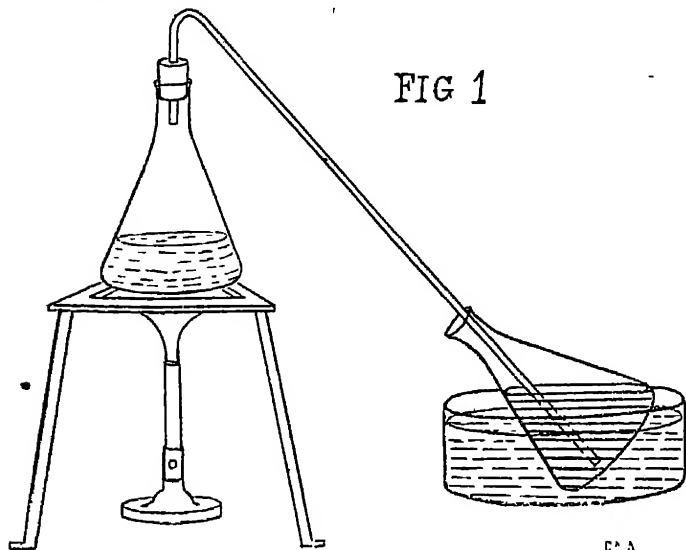
The indicator contains 0.1 gram of potassium ferrocyanide per c.c. of water.

In poorer ores larger amounts are taken, but in no case as much as will contain more than about 0.2 gram of arsenic.

Procedure B

In cases of minerals containing only small quantities of Arsenic, or where it is to be estimated as an impurity, e.g. in Wolfram, from 3 to 5 grams are taken to complete dryness in a beaker flask of 250 c.c. capacity with 10 c.c. pure HNO_3 . Then 5 c.c. of a saturated solution of ferrous sulphate are added, and the assay allowed to simmer for ten minutes. Cool completely, and transfer the whole to a 500 c.c. round flask with 100 c.c. pure HCl , using successive portions of the acid, and, if necessary, using a policeman to detach adhering parts of the assay. Then add 10 grams ferrous chloride and 5 grams calcium chloride. Make a solution of caustic soda by dissolving 30 grams in water, and making up to 150 c.c. in a 500 c.c. round flask. Add a drop of methyl orange indicator solution. Distil the assay into it, keeping it in a vessel of cold water, until the indicator shows it beginning to turn acid. Cease distilling at once. The distillation is done directly into the soda solution. The operation

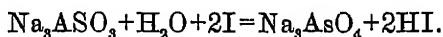
may be performed as in the illustration (Fig 1) Immediately the heat is removed at the end of the distillation, the tube is raised above the level of the liquid and washed in with a few c c of distilled water The solution is cooled, made distinctly acid with 1-1 pure HCl, neutralized with pure NaHCO_3 , and 3 grams in excess added Two c c of starch solu-



tion are added, and the assay titrated with a standard solution of Iodine till a permanent blue coloration is formed The standard solution of Iodine is prepared by dissolving 6.732 grams of Iodine in water with 10 grams KI, and making up to 1 litre Place the Iodine and the KI in the litie flask, and just cover with distilled water Rotate till dissolved and make up to the mark Standardize with pure As_2O_3 Each

c c equals approximately 0 002 gram of arsenic Dissolve 0 1 gram As_2O_3 , equal to 0 0757 gram arsenic in about 0 5 gram pure NaHO in 10 c c H_2O in a 300 c.c conical flask, boiling to complete solution Wash down sides with about 50 c c cold water, render just acid to litmus paper with 1-1 pure HCl , add 3 grams pure NaHCO_3 , make the bulk to about 200 c c with cold water, and titrate in the cold after adding the 2 c c starch solution

Always run a " blank " distillation with the same amount of the reagents used in the assay, and subtract the c c required, if any, from those required by the assay



In performing the above titration, run a preliminary assay or duplicate, to see about how much I solution is required, and in the case of the final assay and standard defer the addition of the starch till all the Iodine solution is run into within 1 or 2 c c of the finish The end point is thereby sharpened Use fresh starch solution daily. The author has used this method for rich ores, using 0 4 gram of the sample, with complete success

BARIUM

The two most commonly occurring minerals of Barium ore are Barytes, a sulphate of sp gr 4 3-4 6, hardness 2 5-3 5, streak white; and Witherite, a carbonate, sp gr 4 3, hardness 3-3 75, and streak white The carbonate of Barium is soluble in HCl , but in the case

751

549.133

1124.

of the sulphate, it is necessary to resort to fusion in order to dissolve it. The fusion is best done in platinum. Should any element detrimental to platinum be suspected, the ore is first given an acid treatment. A gram of the agated sample is weighed into a 250 c c beaker flask, 10 c c pure HNO_3 added, and boiled gently down to dryness, cooled, and 10 c c pure HCl added and boiled to about half bulk. Add 20 c c hot water, allow to settle, filter into a 400 c c conical flask through a 12.5 cm fine paper, and wash with hot water. The BaSO_4 remains insoluble, any BaO or carbonate will go into solution. The next operation is to recover this. Nearly neutralize the assay with $(1-1)\text{NH}_4\text{HO}$. Dilute $\text{H}_2\text{SO}_4(1-1)$ is now added to the boiling solution until no further ppt forms, and the solution boiled rapidly for twenty minutes. It is then allowed to settle till the liquid is quite clear, and filtered off through a 9 or 12½ cm fine paper, and carefully washed three or four times with hot water. This ppt. is dried, the portion insoluble in acid is also dried, and the two are ignited together in a platinum crucible. When completely ignited, four grams of a mixture of equal parts of K_2CO_3 and Na_2CO_3 are added, and the whole mixed in the crucible with a stout platinum wire, and then heated with a cover. Increase the heat till the mass fuses, finishing off with the blowpipe. When cool, the fusion is dissolved out with cold water and the barium carbonate, etc., filtered off through a 12½ cm fine paper, and washed free from sulphates. The residue is washed off the opened paper into a 250 c c beaker flask, 10 c c 1-1 pure HCl poured over it, the paper again washed, and the solution warmed up to near boiling. If it is not clear,

filter into another 250 c c beaker flask, through a 9 cm fine paper, and wash well with hot water. Render the solution alkaline with 1-1NH₄HO, then neutralize with 1-1CH₃COOH, and add 2 c c in excess. The solution is heated to about 90° C, and a strong solution of K₂Cr₂O₇ is added till no further ppt forms. It is allowed to settle, and filtered off through a 12½ cm fine paper, and washed well with a 20% solution of ammonium acetate. Dry, and ignite in a porcelain or silica crucible to barium chromate BaCrO₄. Weigh when cold. The factor for Barium is 0.6047. Log of factor $\bar{1}$ 78154.

BISMUTH

This metal is generally found in the native state, but is found in many minerals in varying proportions. Bismuthine, sp gr 6.4-6.5, hardness 2, and streak lead-grey, is a sulphide, and Bismutite, sp gr 6.9, hardness 4-4.5, and streak greenish-grey, the carbonate.

Procedure A

In the case of the metal, take 5 gram, and of rich ores, one gram, and treat cautiously in a 250 c c beaker flask with 10 c c pure HNO₃. When spontaneous reaction ceases, place it on the warm plate, and bring gradually to dryness. Take up with 20 c c pure HCl, and boil down to about 10 c c. Dilute with 15 c c hot distilled water, allow to settle and filter through a 9 cm paper into a 500 c c conical flask. Wash with hot water to which is added about 5 drops

of pure HCl for each wash. Bring the bulk of the filtrate to some 300 c c and pass through it while hot a rapid stream of H_2S to saturation, gently rotating the flask to hasten reduction of the iron and precipitation of the sulphides. Allow completely to settle on a warm spot, and filter rapidly through a $12\frac{1}{2}$ cm fine paper, and wash with hot water, which is acidified with a few drops of pure HCl , and saturated with H_2S , till the filtrate gives no reaction for iron. Wash back the ppt into the flask, preferably by tilting the funnel, that the same paper may be used for the next filtration. Digest the ppt with 20 c c of strong K_2S solution on the warm plate for ten minutes, bringing it just to the boil. Allow to settle, and filter off through the same paper, and wash with hot water containing a c c. or two of the K_2S solution with each wash, until the filtrate is not coloured, or only very slightly so. Wash the ppt off the opened paper into a 250 c c beaker flask, pour over the paper 10-15 c c. pure HNO_3 , which has been warmed in the flask from which the assay has just been filtered. Rinse the flask with 5 c c hot water, and pour it over the paper, and wash the paper thoroughly. Remove funnel, washing down the stem. Boil down the assay till the separated sulphur runs into globules, and continue evaporation carefully till the assay is dry. Allow to cool, and add 25 c c dilute H_2SO_4 (10 c c pure H_2SO_4 , 15 c c water) and boil down till fumes of H_2SO_4 are evolved continue so for ten minutes. Allow to cool very gradually, add slowly 30 c c cold water. If there is a precipitate here, the assay should be warmed up and frequently rotated to dissolve up any Bismuth separated out. If the solution is clear, proceed without

further warning Cool thoroughly, and allow to stand for two hours Any Lead in the ore will be precipitated here Filter it off into a 500 c c beaker flask, through a 9 cm paper, and wash with a cold 5% solution of H_2SO_4 some six or eight times Add excess of pure (1-1) NH_4OH Bring gradually to the boil, carefully preventing a violent frothing up Boil slowly for two minutes, allow to settle completely, and filter through a $12\frac{1}{2}$ cm fine paper, and wash with hot water till the washings give only slight reaction for sulphates Wash ppt back from the opened paper, pour over the paper some 5-8 c c pure HNO_3 , wash it down thoroughly with hot water, bring the assay to the boil till all Bismuth Hydrate is dissolved, and filter off any sulphur through a 9 cm fine paper, and wash thoroughly with hot water containing a few drops of pure HNO_3 Neutralize the acid largely with NH_4HO (1-1), and add a slight excess of $(\text{NH}_4)_2\text{CO}_3$. Boil off most of the excess, allow to settle, filter through a $12\frac{1}{2}$ cm fine paper, and wash four or five times with hot water Dry the ppt completely at 100°C , separate on to a clean clock-glass as much of the ppt as possible, and ignite the paper in a weighed porcelain or silica crucible Allow it to cool, and add 2 drops of pure HNO_3 Warm gently, and evaporate without spitting, increase the heat gradually till fumes are driven off, and the residue assumes a pale buff colour Allow to cool, and add the ppt Ignite it, at first gently, and increase the heat to dull redness, maintaining this heat till all the ppt has assumed a buff colour Allow to cool and weigh when cold as Bi_2O_3 The factor for Bismuth is 0.8966 Log of factor 1.95269 The above procedure may be used

for poorer ores, on larger amounts of the sample (say 3-5 grams) Where very small amounts are to be determined use the colorimetric Procedure B

Procedure B

Use 2 grams of the sample, and proceed as in Procedure A, to the separation of the Lead To the filtrate from the Lead add an excess of ammonia, filter through a 9 cm paper, and wash out Copper Remove funnel to a 50 c c Nessler tube, pour over the funnel from the beaker flask 5 c c of dilute H_2SO_4 (1-3) and wash with hot water till the bulk of liquid reaches some 40 c c Cool, and bring the bulk up to the 50 c c mark Add one crystal of sodium sulphite, the size of half a pea, and one of KI the size of a pea, and rotate till both are dissolved Bismuth causes a yellow colour in the solution, due to solution of Bismuth Iodide in excess of KI A standard solution is prepared by dissolving 0.1 gram of Bismuth of known purity in just enough pure HNO_3 taking to dryness, and taking up with a couple of c c H_2SO_4 , and diluting to 1,000 c c Each c c equals 0.0001 gram Bi A standard tube is prepared with the same quantities of H_2SO_4 , Na_2SO_3 , and KI and water, and the standard solution run into it till the depth of colour is the same as in the assay tube

CADMIUM

The chief mineral of Cadmium is Greenockite, a sulphide CdS It is rare Its sp gr is 5, hardness 3.5, and streak orange Cadmium occurs in many ores

of Zinc Dissolve a gram of the sample in a 250 c c. beaker flask, and take to dryness with 10 c c pure $\text{HN}(\text{O})_3$. Take up with 10 c c pure HCl , and boil for five minutes. Dilute the assay to 150 c c with hot water, and pass a stream of H_2S to saturation. Allow the sulphides to settle, filter through a $12\frac{1}{2}$ cm paper and wash out iron, etc., with hot, very slightly acidified (HCl) water. Wash the ppt into the original beaker by tilting the funnel, and digest it with a solution of 2 grams of soda in 20 c c water for five minutes, dilute to 100 c c and filter through the same paper, and wash with warm water till colourless. The ppt is now washed back into the beaker flask, and 20 c c of dilute (4-1) pure H_2SO_4 poured over the paper, and the paper well washed. The assay is boiled for ten minutes, allowed to settle, filtered and washed. Cadmium is in solution, add 1-1 NH_4OH till most of the acid is neutralized, dilute to 400 c c with water, and saturate with H_2S while hot. Allow to settle and filter through a $12\frac{1}{2}$ cm fine paper which has been washed with about 10 c c hot water, acidified with HCl , and finally plain water, dried and weighed. Wash with hot H_2S water, acidified with a drop or two pure HCl . Place the funnel with all the precipitate in the fume cupboard, and pour gently all around the top of the paper carbon bisulphide till a drop of the filtrate gives no residue of S when evaporated. Dry the paper with Cadmium sulphide at 100°C in the oven for an hour, cool and weigh. Subtract weight of the paper. The factor for Cadmium is 0.7778. Log of factor $\bar{I} 89187$.

CALCIUM

Carbonate of Calcium in various rocks like chalk and limestone is very common, and as a mineral, Calcite Sp gr 27, hardness 3, streak white Other forms are Fluorite, the fluoride, Apatite, phosphate, Gypsum, a sulphate

Procedure A

In the case of good samples of a carbonate, place 0.5 gram into a 250 c c beaker flask, and add 5 c c pure HNO_3 . Take to dryness. Take up with 10 c c pure HCl , and boil for five minutes. Dilute to 100 c c with distilled water, bring to the boil, and pass a stream of H_2S . Filter off any ppt into a 400 c c conical flask and wash well with hot H_2S water. Boil the filtrate free from H_2S , add 2 or 3 c c pure HNO_3 , and boil for a further five minutes. Separate the Iron as basic acetate (see Iron, Procedure C), filtering into a 750 c c conical flask, dissolving the acetate ppt and reprecipitating as hydrate with dilute NH_4HO . A drop or two of Br is added to the filtrate from the acetate before the ammoniacal solution is filtered into it. This, if any ppt occurs, is brought to the boil, allowed to collect, and filtered off through a 9 cm fine paper into a 750 c c conical flask. The filtrate must be freely alkaline with NH_4HO . It is next treated to a stream of H_2S , and any ppt of Nickel, Cobalt or Zinc which may possibly occur is filtered off and washed. The filtrate is boiled, and Ammonium Oxalate is added in the solid form or as a saturated solution till no further ppt forms, and the assay boiled

for twenty minutes to half an hour. If all the NH_4HO is expelled, add 5 c c and boil for a further five minutes. Allow to settle, and filter off through a $12\frac{1}{2}$ cm fine paper, and wash well with hot water. Dry and ignite gently in a weighed porcelain or silica crucible at a heat under redness. Allow to cool, add 0.5 c c strong $(\text{NH}_4)_2\text{CO}_3$ solution, and dry completely in a water oven. Ignite very gently again till no more $(\text{NH}_4)_2\text{CO}_3$ is evolved, allow to cool in a desiccator and weigh as CaCO_3 . The amount of CaO is usually returned and is got by multiplying the CaCO_3 figure by 0.56. The factor for CaO into Ca is 0.7143. Log 1.85387.

Procedure B

In the case of Gypsum, the ore is fused in a platinum crucible with Na_2CO_3 and K_2CO_3 in the same way as Baiytes (see above, page 30). The CaCO_3 is filtered off and washed as in the case of Barium. It is dissolved in pure HCl , the solution rendered alkaline with 1-10% NH_4HO , and the Ca precipitated as oxalate, and continued as in Procedure A.

CHROMIUM

The chief ore of Chromium is Chromite or "Chrome Iron Ore". Sp gr 4.3-4.5, hardness 5.5, and streak brown.

Procedure A

In the case of rich ores going from 40% to 60% Cr_2O_3 ,

agate the sample finely Place in the bottom of a nickel crucible of about 40 c c capacity a layer of Na_2CO_3 , say about 0.25 gram Then about half fill it with Na_2O_2 , and weigh up 0.5 gram of the sample Place this on the Na_2O_2 , cover the crucible with a nickel lid, and fuse over a Bunsen burner, beginning at a low heat, and increasing the temperature as the material melts, and maintain finally at a dull red for three or four minutes Rotate the molten mass occasionally Allow to cool, wash in the lid with hot water into a 350 c c beaker flask, place in the vessel 40 c c warm distilled water, and then the crucible cautiously in an inclined position, to allow the water access to the fusion Cover the beaker and allow to stand in a warm place until all is dissolved away from the nickel Remove the crucible with tongs, and wash it in thoroughly Bring the bulk to some 150–200 c c, and allow to boil gently for ten minutes Allow to settle and filter off through a $12\frac{1}{2}$ or 15 cm fine paper into a 250 c c conical flask, and wash two or three times with hot water Wash back the ppt into the beaker flask, open out the paper and pour over it into the beaker 20 c c dilute H_2SO_4 Wash in well, and boil till solution is clear, except, perhaps, for silica Now cautiously add a 25% solution of NaOH till alkaline, and 5 c c in excess, and boil gently for five minutes, and allow to settle Filter into the original filtrate through a 15 cm paper, and wash thoroughly with hot water four or five times after the filtrate comes through no longer yellow Reduce the bulk by boiling to some 200 c c and add very slowly dilute H_2SO_4 until the solution is acid, and 20 c c in excess Boil for ten minutes, and cool Add from a 100 c c burette a

decinormal solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, until all the bichromate is reduced. An excess of FeSO_4 solution is shown by a blue colour with potassium ferricyanide on the spotting plate. Add about 5 c c in excess, and note the amount required. Now titrate the excess of iron with decinormal $\text{K}_2\text{Cr}_2\text{O}_7$, using the ferricyanide as indicator. Titrate 50 c c of the FeSO_4 solution with the $\frac{\text{N}}{10} \text{K}_2\text{Cr}_2\text{O}_7$ solution. It will generally be found to be weak due to oxidation of the iron, and must be checked every day it is used. The bichromate solution if made up carefully to $\frac{\text{N}}{10}$ will keep its strength for a long time, but must of course be occasionally checked. Weigh up 1.39 grams of pure $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, dissolve in a 300 c c conical flask in 40 c c dilute H_2SO_4 , and titrate with the $\frac{\text{N}}{10} \text{K}_2\text{Cr}_2\text{O}_7$. If correct it should require 50 c c. The ferricyanide indicator is renewed every day, 2 grams in 100 c c distilled water. Convert the number of cubic centimetres of FeSO_4 solution added to the assay into the equivalent of $\frac{\text{N}}{10} \text{K}_2\text{Cr}_2\text{O}_7$, as found by titration, and subtract the c c of $\text{K}_2\text{Cr}_2\text{O}_7$ required by the excess. Each c c of $\frac{\text{N}}{10} \text{K}_2\text{Cr}_2\text{O}_7 = 0.00254$ gram Cr_2O_3 . For instance 220 c c $\frac{\text{N}}{10} \text{FeSO}_4$ are added, the excess required 9.7 c c $\frac{\text{N}}{10} \text{K}_2\text{Cr}_2\text{O}_7$. $50 \text{ c c } \frac{\text{N}}{10} \text{FeSO}_4 = 48.5 \text{ c c } \frac{\text{N}}{10} \text{K}_2\text{Cr}_2\text{O}_7$. Then $1 \text{ c c } \frac{\text{N}}{10} \text{FeSO}_4 = 0.97 \text{ c c } \frac{\text{N}}{10} \text{K}_2\text{Cr}_2\text{O}_7$.

and 220 c c $\text{FeSO}_4 = 213.4 \text{ K}_2\text{C}_2\text{O}_7$ Subtract the excess = 97 c c $\text{K}_2\text{C}_2\text{O}_7$, then 5 gram sample is equivalent to 203.7 c c. $\frac{N}{10} \text{K}_2\text{C}_2\text{O}_7$ Then 203.7×0.0254 gives the amount of C_2O_3 , if the $\frac{N}{10} \text{K}_2\text{C}_2\text{O}_7$ is correct Suppose it is found to be strong, requiring less than 50 c c to oxidize the iron in 1.39 grams pure $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, say 49.2 c c, then a factor, in this case, $49.2 - 50 = 0.984$ must be used, and conversely if weak The factor for Cr_2O_3 into Cl is 0.6842 Log of factor $\bar{1}83519$

COBALT

Cobalt is mostly found in arsenides, in Smaltite of sp gr 6.4-6.6, hardness 5.5-6, and streak greyish-black, and Cobaltite sp gr 6-6.5, hardness 5.5, streak greyish-black

The arsenic is roasted off before acid treatment Place in a silica or porcelain crucible 1 gram of a good ore, or 3.5 grams of poorer ones, and ignite over a small flame till no more fumes appear to come off, increase the heat somewhat and continue till no more Arsenic is smelt Transfer to a 250 c c beaker flask when cold, boiling out the crucible with 10 c c pure HCl , and washing and policemaning it in Add 5 c c pure HNO_3 and take down to dryness Take up with 10 c c pure HCl , boil for ten minutes and dilute to 100 c c, neutralize with 1-1N H_4OH to a faint ppt, clear with pure HCl , and pass a stream of H_2S till saturated and smelling strongly Allow completely to settle on a

warm part, filter into a 400 c.c. conical flask and wash well with hot water and H_2S . Boil down the filtrate till free from H_2S , oxidize with HNO_3 till no further darkening takes place, and boil again for five minutes. Precipitate the iron, etc., as basic acetate, as described in "Iron, Procedure C," dissolve ppt. in HCl , and reprecipitate as acetate, filtering the second precipitation into the first filtrate. Use a 750 c.c. conical flask. To the filtrate add about one c.c. Bromine. Dissolve the acetate precipitate again in pure HCl , boil till clear, and add excess $1\text{-NH}_4\text{HO}$, and boil again. Filter this into the brominated solution, and wash four or five times. Add ammonia to the solution till all the Br is taken up, bring it to the boil, allow to settle, filter and wash through a 9 cm. or $12\frac{1}{2}$ cm. fine paper into a 750 c.c. conical flask. Into the hot filtrate pass H_2S for thirty minutes. Allow the ppt. to settle, after a thorough agitation, and filter it off, pouring through the $12\frac{1}{2}$ fine paper as much as possible of the liquid without getting the ppt. on the paper. Wash once by decantation with $(\text{NH}_4)_2\text{S}$ water, washing also the paper around once. Now get the ppt. on the paper, and allow the liquid to sink through, but do not wash. Wash the ppt. from the opened paper into a 250 c.c. beaker flask, place 10 c.c. pure HNO_3 into the flask from which the ppt. was filtered, and bring it to the boil. Pour it over the paper into the beaker flask, rinse out the flask twice with hot water, and wash the paper. Boil the assay down till the sulphur runs into globules, and evaporate most of the acid. Add 10 c.c. hot water, and filter off the Sulphur through a 9 cm. fine paper into a 250 c.c. beaker flask, and wash with hot water eight or ten times. Add to the solution a strong

solution of KHO till alkaline, and then make it acid with CH_3COOH . Now add a saturated solution of KNO_3 , some 20–25 c c. Test the solution to see that it is acid, and if not, make it so with further CH_3COOH . Agitate the assay and allow it to stand overnight in a warm place. Filter off the double nitrate of Co and K through a $12\frac{1}{2}$ cm fine paper into a 300 c c conical flask, and wash it six or eight times with a 10% solution of $\text{C}_2\text{H}_3\text{O}_2\text{K}$. Now wash out the $\text{C}_2\text{H}_3\text{O}_2\text{K}$ with alcohol, and dry the ppt carefully at 100°C . Separate as much as possible of the ppt from the paper, and burn it in a weighed porcelain or silica crucible. When ignited, add the ppt after cooling, and then just cover the ppt in the crucible with strong pure H_2SO_4 . The ppt then becomes $2\text{CoSO}_4 \cdot 3\text{K}_2\text{SO}_4$. Evaporate off the excess of acid without spitting on the hot plate, and finish off gently over a small flame till no further fumes come off. The ignition is to be only sufficient to drive off the acid and just fuse the sulphates. Allow to cool and weigh. Factor for Co is 0.1417. Log of factor $\bar{1}4922$.

The procedure may be followed for all ores, two or three grams being taken for poor ones.

COPPER

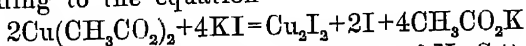
This metal occurs native in considerable quantities. The chief ores are Copper Pyrites, a sulphide with pale green streak, hardness of 3.5–4, and gravity 3.9–4, and Malachite, a carbonate of Copper.

Procedure A

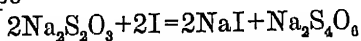
When assaying a rich ore of copper take one gram of the sample, of poorer ores from 2 to 5 grams, and place in a 250 c c beaker. Add 0.2 gram KClO_3 in the case of sulphide ores, but omit it in other cases. Then add gradually, warming slightly at each addition, 20 c c pure strong HNO_3 . When all is added, and spontaneous evolution of brown fumes ceases, boil gently, taking down to complete dryness, and shaking the beaker around occasionally. When dry, cool, and add 30 c c pure strong HCl , and boil down to some 15–20 c c. Dilute to 100 c c, boil, allow to settle and filter through a fine paper (a 9 cm paper will generally be large enough, if not, then a $12\frac{1}{2}$ cm one) into a 750 c c conical flask. Wash well with hot water. If any sulphur remains after opening up, and is not quite yellow, it should be retained in the beaker, while as much as possible of the siliceous insoluble matter is washed on to the paper at the second or third wash. The sulphur is treated with 0.1 gram KClO_3 , and 5 c c pure strong HNO_3 . It is brought gradually to dryness on the hot plate, being frequently agitated so long as the sulphur tends to run into a globule. When dry, add 10 c c pure strong HCl , and boil to half bulk, dilute, and filter through the original paper. When the insoluble matter is thoroughly washed, the bulk is brought to some 400 c c and the assay boiled. H_2S is passed through it to saturation, the liquid being swung around in the flask, to hasten and facilitate the reduction of the chloride and subsequent precipitation of the copper, which comes down as a black sulphide. When saturated, the assay is removed from the H_2S apparatus, and the tube delivering the gas carefully washed

111 Particles of sulphide often adhere to the tube, and may be removed by rubbing with a match-stem, or damp filter paper and washed into the assay. The ppt is allowed to settle, after a thorough shaking, and filtered through a $12\frac{1}{2}$ cm fine paper, the liquid being decanted off, and the ppt washed once or twice by decantation. Hot H_2S water is used, which has been acidified slightly with a drop or two of pure HCl . The ppt is finally washed on the paper, and washed till free from iron. If the filtrate does not smell strongly of H_2S , it should be tested with a further stream of the gas. Any ppt is added to the main bulk. The ppt is washed back into the flask, 10 c c strong HNO_3 is poured over the paper into the assay, and it is washed in with hot water. The paper may be dried and ignited, and the ash added to the assay in the flask. The assay is now boiled down till the sulphur runs into yellow globules, and the bulk of acid may be reduced to 5 c c or so. It is then removed from the heat, agitated to break up the globules, and immediately a stream of air is directed into it, or the assayer blows into it through a bent tube to blow out brown fumes of oxide of nitrogen, as these interfere with a subsequent operation. The flask is rinsed around with cold water, the fumes again blown out, the bulk brought to some 150 c c and cooled. Pure Na_2CO_3 or NaHCO_3 is added in the solid until a slight but distinct apple-green ppt is formed. It is cleared with acetic acid, B P, and 2 c c in excess added. Then add crystals of KI to the extent of ten times as much as there is copper in the assay. (Suppose the ore under examination is Cu_2S , which carries nearly 80% Cu, then the amount of KI to be added is 8 grams.) Iodide of copper is formed

with liberation of a proportionate amount of iodine, according to the equation



It is titrated with a standard solution of $\text{Na}_2\text{S}_2\text{O}_3$. The solution is run in till much of the brown coloration is discharged, when 2 c c starch solution are added, and the titration continued till the colour is finally discharged. A little practice will soon enable the operator to find the exact end-point. An excess of hypo shows a watery spot. When the blue of iodide of starch is discharged the iodide of copper is dissolved in excess of hypo



The standard solution of hypo is made by dissolving 39.18 grams pure $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in distilled water and making up to a litre. It is standardized with pure electrolytic copper. It is a good plan to take as much copper for the standard as is found in the ore. Each c c of standard hypo equals about 0.01 gram copper.

Procedure B

An excellent method for good ores, but one in our experience tending to give slightly lower results than Procedure A, is to take the ore up, after taking dry with HNO_3 , with 20 c c 3-1 dilute H_2SO_4 , and boil down till fuming. Allow to fume for five minutes, allow to cool gradually, dilute to 100 c c with water, boil for five minutes, allow to settle, filter into a 750 c c conical flask and wash thoroughly with hot water. Bring the bulk to some 400 c c and boil. Now add, at the rate of 2 or 3 c c at a time, a boiling saturated solution of $\text{Na}_2\text{S}_2\text{O}_3$ and shake the assay thoroughly

between each addition When all colour is gone from the solution, and the sulphide of copper settles rapidly to the bottom, a further addition of hypo makes no change and the precipitation is complete After a very thorough final agitation, the ppt is allowed to settle, and rapidly filtered as soon as settled through a $12\frac{1}{2}$ cm fine paper, and washed with hot water and a few drops of H_2SO_3 till free from Iron It is then washed off the paper as in the case of the H_2S precipitation of Procedure A and that procedure followed to the end

Procedure C

The ore is treated as in Procedure A or B as far as boiling down the nitrate solution till sulphur runs into globules The bulk is not reduced after this It is diluted to 150 c c with cold water, 30 c c 1- NH_4HO is added, and the solution titrated with a standard solution of KCN till the blue colour is discharged A standard is run with pure electrolytic copper, and the success of this method depends upon the amounts of materials used, bulks of solution and all conditions being the same The globules of sulphur in the assay may be neglected The standard is run immediately after the assay In an ore going 50% of copper, for instance, 0.5 gram electrolytic copper is weighed into a 750 c c conical flask, and dissolved in 10 c c pure HNO_3 Boil for two minutes, dilute with cold water to 150 c c, add 30 c c 1- NH_4OH , and titrate as nearly as possible at the same rate as the assay

The standard solution of KCN is made by dissolving 42 grams of it in distilled water, and making up to a litre 1 c c = 0.01 gram Copper

Procedure D

In the case of ores containing much impurity, e.g. Sb, As, 3-5 grams are taken, according to richness of the sample, and Procedure A is followed to washing the sulphide ppt free from I₂ion. The ppt is then washed back into the flask by tilting the funnel, and not opening the paper. Then 20 c.c. of a strong solution of K₂S (prepared by passing a rapid stream of H₂S through a strong solution of KOH) is added, the assay brought to the boil, and filtered through the same paper, and washed with hot water with a few drops of K₂S solution at each wash until the solution is colourless. The ppt is then washed back, dissolved in HNO₃ as in Procedure A, and so on to the end.

If the ore contains much Pb it is taken up with H₂SO₄, when the bulk of the Pb is precipitated as sulphate, and filtered off with the insoluble matter.

Procedure E

When estimating very small quantities of Cu, a colorimetric process is adopted. Take 5 grams of ore, and follow Procedure D. The solution of the sulphides in HNO₃ is taken very low, it is diluted with distilled water to 20 c.c. Add 8 c.c. NH₄HO (1-1), bring nearly to the boil, and filter through a fine 9 cm. paper into a 100 c.c. Nessler tube, and wash. If much ppt (Bi) is present, it must be dissolved in HNO₃ and reprecipitated with ammonia NH₄HO, and filtered and washed again. Another tube is prepared with as nearly as possible the same amounts of water, acid, and NH₄HO, and the tubes cooled. To the standard tube, standing with the assay tube on a white surface (tile or paper) is added a standard solution of Cu until the depth of

colour is the same as in the assay tube. The bulks should both be at the 100 c c mark, and the matching done as nearly as possible. It is nearly always the case that the assay tube will appear a more greenish-blue than the standard. If a drop or two of a very dilute solution of K_2CrO_4 is added to the standard tube, the same greenish tint is given to this one, and the colours more satisfactorily matched.

The standard solution is made by dissolving 0.5 gram electrolytic copper in sufficient HNO_3 , boiling for a minute and diluting to a litre. Each c c = 0.005 gram Cu.

GOLD

A general indication of the procedure of the assay of Gold ores only, is given here.

The method used is a dry one. The principle is the collection in a "shower" of Pb of the gold through the fusing ore. The chief constituent of the gangue of gold ores is most often quartz. The flux for this is Na_2CO_3 .

$SiO_2 + Na_2CO_3 = CO_2 + Na_2SiO_3$, so that theoretically 60 parts SiO_2 require 106 parts of Na_2CO_3 . Litharge, PbO , also fuses it well, and is used in conjunction with the Na_2CO_3 . The button of Pb is got by the addition of charcoal (or flour), which reduces the PbO to Pb. About twice as much flour is required as charcoal, and is sometimes preferred. It is finer, and easier to mix in the charge.

The weight of ore generally used in this case is the "assay ton". Results are returned either in ounces

and decimals of an ounce, or ounces, penny-weights and grains per ton. The ton may be the usual or "long" ton of 2,240 pounds, or the "short" one of 2,000 pounds. In the case of the long ton a convenient weight for the assay ton is 32 6667 grams, since there are 32 6 ounces to the long ton. It will be seen that each 0 001 gram of gold from a charge of one assay ton of ore equals one ounce of gold per ton, a corresponding weight for the short ton is 29 1667 grams. The object of the assay is to get a flux which will gradually fuse the ore to a syrupy mass, through which the Pb may run to form a button of convenient size, the whole poured into a mould when completely fused and tranquil, and the solidified slag knocked away when cold from the button of metal. The button is cupelled in a muffle furnace in which the Pb is oxidized and absorbed into the cupel, leaving the bead of Gold. For a highly siliceous ore the following proportions of fluxes will give a good fusion for one assay ton of ore (long or short)

Ore	1 assay ton
Na_2CO_3	64 grams
$\text{Na}_2\text{B}_4\text{O}_7, 10\text{H}_2\text{O}$	6 5 grams
PbO	48 grams
Flour	2 5 grams

Place the ore, with the Na_2CO_3 and $\text{Na}_2\text{B}_4\text{O}_7$, in a clean Wedgwood mortar. Mix them thoroughly, add the PbO and flour, and mix again. Turn the charge out on to a piece of glazed sampling paper, and transfer to a crucible known as a "Battersea Ground". Place in a furnace at a red heat, having first put a cover on the crucible. Increase the heat till the whole mass

fuses, and when tranquil, take off the cover, remove the crucible, swing it gently around to "wash" any particles of Pb into one mass at the bottom, and pour carefully into a clean *dry* mould. When cold knock away the slag, knock the button into a cube and knock off any adhering slag. The next step is to cupel the button. This is done in a muffle furnace, one in which reducing gases do not play on the assays, but they are heated in a compartment to which the oxygen of the air has free access, thus oxidizing the lead and leaving gold and silver in the cupel. The muffle furnace must be brought to practically a bright orange heat with the cupel in position, and the button of Pb placed gently into it, the mouth of the furnace immediately closed, and allowed to remain so until the button is melted and had time to reach its maximum heat when the upper part of the furnace mouth is cautiously opened an inch or so, and gradually removed altogether. It is important to avoid a sudden inrush of cold air. This would cause "freezing," or a formation of a crust of oxide on the top of the metal which prevents further cupellation. If this should happen, cupellation may be restarted by holding over the cupel just above the crust a piece of charcoal, or by cautiously dropping a little charcoal on the top, and reclosing the furnace mouth. The crust will be reduced when cupellation may again begin. The course of the cupellation can be seen by a gradual diminution in size of the molten metal, and the final bead of precious metals is easily distinguished from the cupelling lead. When finished the cupel is brought to the front of the furnace, and finally withdrawn altogether. When cold the bead is

gently prised from the cupel with a pair of forceps, placed on a clean smooth anvil and given a tap with a hammer to flatten it. It is thus also freed from any speck of adhering cupel, which is brushed away. The bead is then weighed. The gold is always alloyed with silver from which it is "parted" by treating in pure dilute HNO_3 , in which gold is insoluble while silver goes into solution. The silver, however, must be present to the extent of at least 25 times the amount of gold to part properly. A yellow bead will be sure to require the addition of pure Ag to give a proper parting. Weigh up 25 times the weight of the bead in a gram or two of lead foil and cupel it with it. Flatten on the anvil as much as possible, and, if wider than a test tube, curl it till it will drop easily into one. Add 10-15 c c of "first" parting acid, which is one part of pure redistilled HNO_3 to one of distilled water. No trace of Cl must be present or gold will go into solution. The test tube is kept in a vessel of boiling water for twenty minutes. It is then removed, the acid is poured off the residue slowly, to allow it to remain in the tube. Then a similar amount of stronger acid is added to it of the strength of one part of acid to half of distilled water. This is given twenty minutes in the boiling water, the acid poured off, and the residue given two or three careful washes with distilled water. The tube is then filled with water, a small crucible (preferably of clear fused silica) of deep narrow shape is placed over the top, and the whole quickly inverted so that the gold drops into the crucible, the test tube is carefully slid away, the edge of the crucible placed against the test tube, and the water poured carefully away, so that

the gold lies in the bottom. It is carefully dried, and gently ignited over a small Bunsen flame, allowed to cool, and weighed. The difference between the weight of the original button, and that of the gold, gives the weight of silver.

The gangue of gold ores may contain oxides and sulphides of different metals, requiring different fluxes and treatment.

Oxide of Iron occurs frequently, borax and litharge fuse it. An increase of flour is necessary in oxidized ores. With many ores a good plan is to run a preliminary assay with a view to getting a malleable lead button of correct weight. This should be from 20 grams to 25 grams.

In the case of sulphides occurring in any quantity the ore is roasted in an open clay dish before fusion. This may be done at the mouth of the muffle at incipient redness. When the preliminary fumes have been driven off, the ore is stirred with a clean iron rod, and treated till no further SO_2 can be smelted on withdrawing the dish. The sulphides are thus principally converted into oxides. If the ore contains not more than, say 10% of sulphides, it may be fused right away, the sulphides taking the place of flour in reducing PbO . To ensure a malleable button insert in the assay pot two or three iron nails (say 3 inch). When the ore is fused, stir it around with each nail, and tap any buttons of Pb off them before pouring the assay. The remarks on metallics in Part I do not apply to gold ores. In this case the weight of ore from which they were obtained is determined. The metallics themselves are wrapped in lead foil, and cupelled, inquarted, and parted. The yield

of precious metals as metallics is calculated from their weights in relation to the weight of ore from which they were obtained, and this result added to the return from the metallics-free ore, which is fused and assayed in the usual way separately

In the case of rich ores it is necessary to collect the slag from the first fusion and retreat it with fresh litharge and flour, for gold which has not been collected in the first button. The resulting button is cupelled, and the bead, if any, treated as above, the results being added to those of the original fusion. Sometimes a Pb button too big for the cupel is obtained, or it is brittle carrying Cu, or some other base metal, which will interfere with cupellation or cause loss of gold. Such buttons are scorified. The temperature required for this operation surpasses that required for cupellation. The button is scorified with a gram or two of borax. A ring of litharge forms on the lead as the operation proceeds, which becomes thicker and thicker until a layer forms right over the Pb, and the fusion poured into a dry mould, and the button treated as above.

Some complex ores, and very rich ores, are assayed by scorification. Only one-tenth of an assay ton can be taken, and 30 to 40 grams of granulated Pb free from Ag, or of which the Ag content is known and can be deducted. The ore is mixed with half the Pb. This is placed in the scorifier, and the rest of the Pb is spread on the top, and a gram or so of borax placed on this, and the whole scorified. The slag is "cleaned" by dropping on to the molten assay in the muffle when the ring has closed about 0.5 gram of charcoal wrapped in tissue paper, and closing the

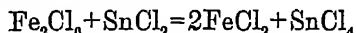
muffle for a few minutes before withdrawing the assay. Several scorifications can be done, the resulting buttons scorified together to a convenient size, if it is desirable to work on a larger amount of ore

IRON

This metal occurs chiefly as oxide. Hæmatite, sp gr 5.5–6.5, streak iron-black, and hardness 5.5–6.5, and Magnetite sp gr 5.1–5.2, streak black, and hardness 5.5–6.5 are the chief oxides. Chalybite is a carbonate of sp gr 3.8, streak white, and hardness 3.5. There are also the ochres.

Procedure A

Most of the ores of Iron are soluble in HCl. In the case of rich ores take 0.35–0.4 gram of the agated sample, place in a 300 c.c. conical flask, and digest on the hot plate with 20 c.c. pure HCl till showing nothing undissolved but white siliceous matter. Dilute to 150 c.c. with water, and bring to the boil, and add drop by drop to the boiling solution a saturated solution of stannous chloride



until the yellow colour of Ferric Chloride is discharged. Do not add a large excess of the SnCl_2 . An excess of course is necessary, but let it be a small one. This excess is precipitated by adding a strong boiling solution of Mercuric Chloride till no further ppt forms. Bring to the boil, place a cover on the flask, and cool. Titrate with a standard solution of $\text{K}_2\text{Cr}_2\text{O}_7$,

using a solution of Potassium Ferricyanide as indicator on a spotting plate Ferrous iron imparts to the indicator a blue colour which is not the case with the oxidized iron The end of the titration is indicated therefore by the removal of the colour. Much reduced iron imparts a dense blue, which gradually fades as the iron is oxidized The titration may be finished to a drop, an excess of bichromate imparts a straw colour to the indicator It is well to run three assays where the amount of iron is quite unknown, the first one being run slowly with continual spotting, the others run to within a c c or so of the finish, and then finished gradually

$6\text{FeCl}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + 14\text{HCl} = 3\text{Fe}_2\text{Cl}_6 + \text{Cr}_2\text{Cl}_6 + 2\text{KCl} + 7\text{H}_2\text{O}$
 The standard solution of $\text{K}_2\text{Cr}_2\text{O}_7$ is made by dissolving 4.39 grams in distilled water, and diluting to a litre The ferricyanide solution is made fresh each day by dissolving 0.1 gram in 100 c c distilled water

The Bichromate solution is best standardized with pure iron wire Weigh 0.2 gram into a 300 c c flask, and dissolve in 10 c c dilute H_2SO_4 , dilute with cold boiled distilled water to 150 c c and titrate. Each c c equals 0.005 grams Fe

Alternative methods for reducing the iron may be employed When the iron is dissolved, and the solution diluted as in the above Procedure, pass a stream of H_2S through it while hot, till it smells freely of the gas If a ppt is formed it is filtered off, and thoroughly washed with hot water and H_2S Boil the solution till a strip of lead acetate paper no longer darkens in the issuing steam, cool, and titrate as above H_2SO_3 may be used in the reducing agent in H_2SO_4

solution of the iron The excess must be boiled off as in the case of H_2S

Procedure B

Weigh 35 to 4 gram of a rich ore into a 300 c.c. flask, and 5 c.c. pure HNO_3 and take to dryness, add 30 c.c. dilute H_2SO_4 and boil down till fuming begins. Allow to cool gradually, dilute with cold water to 150 c.c., bring to the boil, and reduce as in Procedure A with H_2S or H_2SO_3 . Cool and titrate with a standard solution of $K_2Mn_2O_8$ until a drop colours the solution distinctly pink. This colour may fade, but the end of the titration is reached when the pink colour first colours the whole solution.

The standard solution of permanganate is made by dissolving 2.82 grams in distilled water and diluting to a litre. Standardize with iron wire as in Procedure A.

If pure iron wire is not available, ferrous sulphate, $FeSO_4 \cdot 7H_2O$ of known purity may be used. It contains when pure 20.14% Fe. Take one gram, dissolve in a 300 conical flask in 30 c.c. dilute H_2SO_4 , dilute to 150 c.c. and titrate. If the standard solution is correct it will require 40.3 c.c.

Procedure C

In the case of impure and complicated ores take as much as will contain not more than 0.5 gram of iron, place in a 250 beaker flask, add 10 c.c. pure HNO_3 , and take to dryness. Take up with 20 c.c. pure HCl , and boil for ten minutes. Dilute to 50 c.c. with distilled water, boil, allow to settle, and filter into a 300 c.c. conical flask through a 9 cm. fine paper. If the

residue is suspected of containing undecomposed Fe, it is fused with Na_2CO_3 , extracted with water, taken to dryness with HCl, taken up with HCl, diluted, filtered and washed into the original acid solution. Wash thoroughly with hot water, bring the bulk to 150 c c and pass a stream of H_2S through it to saturation. Filter through a 9 cm or $12\frac{1}{2}$ cm fine paper, and wash with hot water containing H_2S and acidified with a drop or two pure HCl. If the ore contains no further impurities the iron may be estimated in the solution by Procedure A, after boiling off the excess of H_2S . If Mn is present in any quantity or other impurity as Zn, Ni, Co, etc., the "basic acetate" separation is performed. After all H_2S is boiled off (test with lead acetate paper), 5 c c of pure HNO_3 is added, and the assay boiled for a further five minutes. A 20% solution of NaOH is then added until the assay assumes a reddish tint. Then the assay is cooled to about 80°F ., and a saturated solution of Sodium Acetate added until the assay no longer darkens. It is then diluted to about 400 c c and brought to the boil, and at once removed from the heat. Allow to settle. Filter through a $12\frac{1}{2}$ cm fine paper and wash once with hot water. Wash back into flask by opening out the paper, pour over the paper 10 c c pure HCl, wash in well, boil till quite clear, and add a slight excess of 1- NH_4HO , boil again for two minutes and filter off through a $12\frac{1}{2}$ cm fine paper, and wash some six times with hot water. Wash back the ppt again, pour over the paper 10 c c pure HCl, wash the paper well with hot water and boil the solution till clear. The iron is then determined as in Procedure A.

Procedure D

Very small quantities of Iron are estimated colorimetrically, a solution of a sulphocyanide gives to ferric salts in solution a reddish colour, varying in intensity with the amount of Iron present. A standard solution of Iron is prepared by dissolving 0.1 gram of pure Iron wire in sufficient pure HCl, oxidizing with a few drops of pure HNO_3 , taking to dryness and taking up with 3 c.c. pure HCl. The solution is diluted to 1 litre, and each c.c. = 0.0001 gram Iron.

Dissolve 5 grams of Potassium Sulphocyanide in 100 c.c. water.

Iron will be found in practically every mineral, in some in very small quantities, as in China Clay, for example.

The Iron, in the oxidized state and in solution in pure HCl, is placed in a Nessler tube, 10 c.c. of the sulphocyanide is run in, the whole being cold, and made up to the 50 c.c. mark. A standard tube is prepared with cold water and 10 c.c. sulphocyanide, the standard Iron solution run in carefully till the depth of tint is the same, and the bulk made up to the 50 c.c. mark. This test is extremely sensitive and minute amounts of Iron can be determined by it.

LEAD

The commonest mineral of Lead is Galena, sulphide of lead, with a gravity of 7.4-7.6, and hardness 2.5-2.75. It is a dark grey mineral of metallic lustre, and lead-grey streak.

Procedure A

In the case of pure or nearly pure samples of galena, one gram of the 90 mesh sample is treated in a 200 c c beaker with 15 c c pure HNO_3 and about 2 gram KClO_3 and placed on the warm plate till evolution of brown fumes has ceased. It is then boiled slowly down to dryness. If much sulphur remains unoxidized or is of a greenish colour, a further 5 c c pure HNO_3 , together with about 0.1 gram KClO_3 are added, and the assay brought again slowly to complete dryness. Now add 20 c c of 1-1 H_2SO_4 , and boil down until the white fumes of H_2SO_4 evolve, and continue this for ten minutes. Cool gradually, add 20 c c of pure cold water, bring to the boil, cool again, and add an equal volume of alcohol. Allow to stand overnight. Filter off the precipitate and residue through a $12\frac{1}{2}$ cm. fine paper, and wash with dilute H_2SO_4 (strength 1 of acid to 4 of pure water) till free from metals in solution, get the whole on the paper, and wash around the top of the paper six times with alcohol, allowing it to run right through each wash. Now dry the ppt carefully at 100°C and detach as much as possible of it from the paper on to a clean, dry, warm watch-glass. Burn and ignite the paper in a weighed porcelain or silica crucible, allow it to cool, add 2 drops of pure HNO_3 , and warm gently, then 1 drop of 1-1 H_2SO_4 , warm up again, and heat till all the acid is driven off. When cool, add the ppt on the watch-glass, and ignite for ten minutes at a dull red heat. Cool and weigh. This weight represents the PbSO_4 yielded by the sample together with the insoluble matter. The PbSO_4 and insoluble are transferred to a 250 c c beaker, the crucible being boiled out with two-

thuds its capacity of saturated solution of ammonium acetate, the solution added to the beaker and the crucible finally "policed" out. Ten grams of ammonium acetate in 25 c c water are added, and the whole gently boiled until the PbSO_4 is dissolved out. It is filtered and washed with boiling water ten times, a little ammonium acetate being added to each wash. It is finally dried, ignited and weighed. This weight subtracted from the previous one gives the amount of PbSO_4 yielded by the sample. The factor for Pb is 6832. Log of factor $\bar{1}83453$.

Procedure B

In the case of impure Galenas or other ores of lead, proceed as follows:

Take 2-5 grams of sample and add 15 c c pure HNO_3 in a 250 c c beaker with 2 gram KClO_3 , and bring gently down to dryness. Now add 20 c c pure HCl , and boil for ten minutes. Add 20 c c boiling water, and, while quite hot, filter off through a 9 cm or $12\frac{1}{2}$ cm fine paper into a 750 c c conical flask, keeping as much as possible of the insoluble residue in the beaker. Wash six times with boiling water, and finally with 5 c c of a saturated solution of ammonium acetate. This will dissolve out any remaining traces of lead chloride. Get the residue on the paper, and wash finally with boiling water. Let the bulk now be 350-400 c c. Neutralize most of the acid with 1- NH_4HO without getting a permanent precipitate, and bring to the boil. Now pass into the assay a stream of H_2S , while keeping it gently rotating. When the iron, etc., is reduced, let the assay saturate with H_2S for twenty to thirty minutes, when it should smell

strongly of the gas on being disconnected from the generator, and allowed to stand for five minutes. When it has stood in a warm place till quite settled, it is filtered off through a $12\frac{1}{2}$ cm fine paper, and washed free from iron, etc, with hot water to which a few drops of pure HCl have been added, and H_2S water added at each wash. The filtrate should be further tested with H_2S . Wash the ppt back with hot water into a 250 c c beaker and pour over it 20 c c of a strong solution of K_2S , and wash paper with hot water. If any ppt remains on the paper, preserve it, to dissolve the ppt off ultimately with HNO_3 . Bring the sulphide digestion to the boil, allow to settle, filter off through $12\frac{1}{2}$ cm fine paper, and wash with hot water containing K_2S , till the filtrate is colourless. Wash back the ppt into the beaker, pour over the opened paper 10 c c of hot pure HNO_3 into the beaker, and wash off. Take to dryness, and take up with 20 c c 1-1 H_2SO_4 , heat till fumes are evolved, allow to fume for ten minutes. Allow to cool, and proceed as in Procedure A, weighing as pure $PbSO_4$.

MAGNESIUM

The chief mineral of Magnesium is Magnesite, a carbonate of sp gr 3-3.1, hardness 3.5-4.5, and streak white. It occurs in dolomite and limestone. There are several silicates of magnesium, e.g., Serpentine, Steatite, Meerschaum, etc.

Procedure A

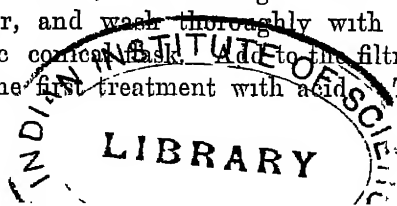
In the case of good samples of magnesite, dissolve 0.5

gram in a 250 c c beaker with 10 c c pure HCl, and boil for ten minutes. Dilute to about 40 c c and filter off through a 9 cm. fine paper into a 200 c c conical flask, and wash thoroughly with hot water. Pass a stream of H_2S through the filtrate to saturation, and, if any ppt is formed, filter off and wash with H_2S water into a 300 c c conical flask. Boil down the filtrate to about 100 c c, add 5 c c pure HNO_3 , and boil again for five minutes. Add 2 grams NH_4Cl and excess of 1-1 NH_4HO , and pass H_2S in a rapid stream for fifteen minutes. Allow to settle, filter off through a 12½ cm fine paper into a 500 c c conical flask, and wash thoroughly with hot water with $(\text{NH}_4)_2\text{S}$ in solution. To the ammoniacal filtrate add a slight excess of $(\text{NH}_4)_2\text{CO}_3$, and allow it to stand for an hour on a warm part of the plate, and filter through a 9 or 12½ cm fine paper, and wash with warm water into a 750 c c. conical flask, bring the bulk to some 500 c c, add 10 c c 880 NH_4HO , and add an excess of a saturated solution of Sodium Phosphate. The assay is thoroughly cooled and agitated energetically for five minutes, and allowed to stand overnight. It is filtered off through a 12½ cm fine paper, and washed free from Sodium Phosphate with cold dilute NH_4HO . Wash the precipitate back into the flask from the opened paper, pour over the paper and into the flask 10 c c pure HCl, and wash thoroughly with hot water. Bring the bulk to 200 c c. and boil till quite clear. Render just alkaline with dilute NH_4HO , and add 5 c c of the stock acetic acid—sodium acetate solution as described under "Arsenic, Procedure A"—and titrate the boiling solution with the standard solution of Uranium acetate (see "Arsenic,

Procedure A"), using the potassium ferrocyanide indicator. Get the arsenic standard for the uranium acetate, and, since Mg in this case corresponds to As, the Magnesium standard is got by multiplying the As figure by 0.3200.

Procedure B

In the case of ores insoluble in acids, e.g. the silicates, the agated ore—5 gram—is fused in a platinum crucible with 5 grams of about equal parts of pure Na_2CO_3 and K_2CO_3 . Should the ore be suspected to contain anything deleterious to Pt, e.g. S, As, etc., it is first treated as in Procedure A, with acid, the solution kept, and the ignited residue then fused. The fused mass is leached out in a porcelain dish (4 to 5 inches in diameter) with hot water, the crucible being finally extracted with about 5 c.c. pure HCl, and "policemanned". Take care to cover the dish with a clock-glass when adding acid. When the mass has been mostly disintegrated, pure HCl is cautiously added till no further effervescence is seen, 5 c.c. in excess added, the clock-glass washed in, and the whole evaporated to complete dryness on a water bath, and then placed in a water oven till no pungent fumes can be smelt, the residue being gently broken up with a stout glass rod. Add 10 c.c. pure HCl, and repeat the drying process. Add a further 10 c.c. pure HCl, 50 c.c. of hot water, and heat till all is in solution save the SiO_2 . Allow to settle, filter through a 9 cm. or $12\frac{1}{2}$ cm. fine paper, and wash thoroughly with hot water into a 500 c.c. conical flask. Add to the filtrate the filtrate from the first treatment with acid. The



magnesium is now all in solution and Procedure A may now be followed from "Pass a stream of H_2S "

Procedure C

In cases where small amounts only of Mg occur, two grams of ore may be taken, the ore decomposed by acid, or if necessary by fusion, and the above procedure followed

MANGANESE

The chief ore of Manganese is Pyrolusite, the black oxide Sp gr 4.8, hardness 2-2.5, and streak black

Procedure A

In the case of good ores weigh 0.5 gram into a 250 c c beaker flask, add 5 c c pure HNO_3 and take to dryness. Add 10 c c pure HCl , and boil till nothing remains but siliceous matter. Dilute to about 100 c c and separate Iron by the acetate method as described under "Iron, Procedure C," filtering into a 750 c c conical flask. The filtrate from the first precipitation is treated with 3 or 4 c c of bromine, and allowed to stand in a warm place some five or ten minutes before the ammoniacal solution is filtered into it. When the Iron precipitate is finally washed, dilute NH_4HO is cautiously added till all the Br is taken up, and an excess is present. The assay is brought to the boil,

and allowed to settle. It is filtered through a $12\frac{1}{2}$ cm fine paper, and washed two or three times with hot water. It is then washed back into 250 c c beaker flask, 10 c c of pure HCl are warmed up in the flask from which the Mn was filtered, and poured slowly over the opened paper. Let the paper stand thus for two or three minutes, when it may be washed free from Mn with hot water. The solution is boiled down to about 100 c c, and a slight excess of pure Na_2CO_3 added. It is then boiled for five minutes, allowed to settle, and filtered through a $12\frac{1}{2}$ cm fine paper, and washed free from Na salts. It is dried and ignited in a weighed porcelain or silica crucible, and when cold, weighed as Mn_3O_4 . Factor for Mn is 7205. Log of factor $\bar{1}85764$.

The above procedure gives the total amount of Manganese in an ore. Where the amount of Mn occurring as MnO_2 is required the following method may be followed.

Procedure B

Dissolve in a 400 c c conical flask one gram of pure Iron wire, or 5 grams pure $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 c c dilute $\text{H}_2\text{SO}_4(4\text{H}_2\text{O}-1\text{H}_2\text{SO}_4)$. When dissolved add 0.75 gram of the agated sample, and warm gently till all the black MnO_2 is seen to be dissolved. Cool the assay, and titrate it with a standard solution of $\text{K}_2\text{Cr}_2\text{O}_7$, as described under "Iron, Procedure A". The result of the titration indicates the amount of Iron unoxidized by the MnO_2 . This amount subtracted from the total amount of Iron used gives the Iron oxidized by the MnO_2 . This amount multiplied by 7768 gives the MnO_2 in the sample. For example

1 0000 gram Fe wire used
 0 1500 ,, ,, remains unoxidized

 0 8500 ,, ,, oxidized by 0 75 grams ore
 $0.85 \times 0.7768 = 0.65028$ grams MnO_2
 $0.65028 - 0.75 \times 100 = 86.70\%$ MnO_2 , or.
 5 grams $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ used equals
 $5 \times 0.2014 = 1.0070$ grams Fe
 0 1570 ,, ,, unoxidized

 0 85 ,, ,, oxidized
 = 86.70% MnO_2

Procedure C

In poor or complex ores, take from 3 to 5 grams, place in a 250 cc beaker flask, and take to dryness with 15 cc HNO_3 . Take up with 20 cc pure HCl , and boil for ten minutes. If the ore is not attacked by acids, resort is made to fusion, or in the case of Wolfram, the agated portion is digested with 20 cc of 30% NaOH solution in a 250 cc beaker flask, on the hot plate till it assumes a syrupy consistency. It is then carefully diluted to about 100 cc with water, 2 drops 40% formaldehyde added, and boiled for two minutes. Allow to settle, filter and wash. Wash back the ppt and residue into the beaker flask, add 10 cc pure HCl , and 5 cc pure HNO_3 , pouring them over the paper. Boil till nothing remains but siliceous matter, filter and wash into a 300 cc conical flask. Now proceed as in Procedure A to ppt Iron, etc., as basic acetate, and so on.

MERCURY

The chief source of Mercury is the red sulphide Cinnabar of sp gr 8.82, hardness 2-2.5, and streak scarlet

Procedure A

Mix in an agate mortar 0.5 gram of the sample with 2 grams Na_2CO_3 and 2 grams of iron scale. Transfer to a porcelain or silica crucible of some 40 cc capacity, "wash out" the mortar with about a gram more of iron scale, and brush it into the crucible to form a layer on top. On the crucible place a gold cover. Imagine a round flat piece of gold of such a size that its edge projects just over the crucible when placed on it. This is given a depression in the middle, which extends nearly to the edge of the crucible inside, and the rim thus made is somewhat elongated at one point to form a handle for grasping it with tongs. Fill the depression with cold distilled water. Place the whole over a small flame which will keep the crucible heated below redness, for ten minutes. Test the temperature of the water occasionally with the finger, and when it becomes warm, remove it with a pipette, and immediately replace it with cold water, so that the gold cap is kept always cold. Mercury is sublimed on to the gold. Remove the heat, carefully pour away the water, wipe the cap dry carefully with filter paper, both in the depression, and, if necessary, the mercury coating. Do not rub the Mercury, just dab it lightly. Place in a desic-

cator for a few minutes and weigh when cold. Sublime the Mercury over a small flame, allow to cool, and weigh the gold. The difference gives Hg on 0.5 gram of ore.

Test the residue by replacing the cap, putting cold water in it, and heating again. Any further Hg is added to the first weight.

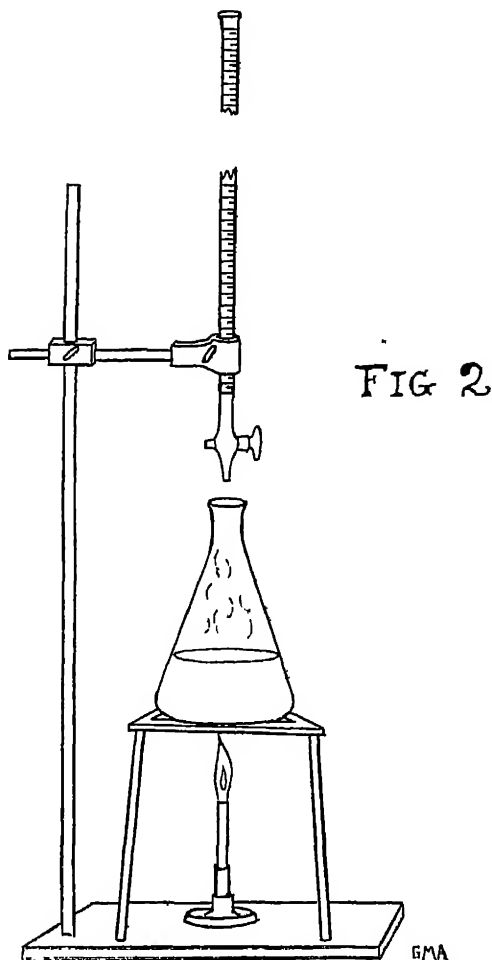
MOLYBDENUM

Molybdenite, sulphide of Molybdenum, is the chief source of Molybdenum. Sp. gr. 4.7-4.8, hardness 1-1.5, streak greenish-grey on porcelain. Another mineral is Wulfenite, molybdate of lead.

Procedure A

In cases of rich samples of Molybdenite weigh 0.5 gram of the sample into a 250 c.c. beaker flask, add 0.3-0.4 gram of Potassium Chlorate, and 20 c.c. pure strong HNO_3 , and place on a slightly warm place, covered with a watch-glass or lid, and constantly blow gently out the oxide of chlorine formed to prevent explosion of the gas. Continue thus till brown fumes begin to be evolved, when the assay may be moved to a warmer part. When spontaneous action has ceased, boil the assay gently, shaking the beaker around occasionally. Boil down to about 5 c.c. and allow to cool. Add 50 c.c. of distilled water, and 2N Na_2CO_3 till alkaline and 15 c.c. in excess. Boil till all the white oxide of Molybdenum is dissolved, allow to settle, filter through a 9 cm., or, if much iron, etc., is present, a 12½ cm.

fine paper into a 750 cc conical flask, and wash six



times with hot water. Wash back the precipitate with residue into the beaker, add 5 cc pure strong HNO_3

and about 0.05 gram Potassium Chlorate, and boil down nearly to dryness. Take up with 20 cc hot water, add 2N Na_2CO_3 again in slight excess, boil, allow to settle, and filter again into original filtrate. Wash at least six times, allowing each wash to sink completely through. Render the filtrate acid with acetic acid, and add 5 cc in excess. Then add 10 grams of ammonium chloride and 50 cc of a 20% solution of ammonium acetate. Bring the assay to the boil, and, while keeping on the boil, add drop by drop, from a burette, excess of a solution of lead acetate (Fig. 2) made by dissolving 40 grams of the salt in distilled water, with 20 cc acetic acid, making up to a litre with water. The amount of lead acetate solution required may be roughly determined if the iron, alumina, etc., and insoluble is collected, dried, ignited and weighed, subtract the percentage found from 100, and call the rest molybdenum sulphide. This figure multiplied by 0.6 gives the equivalent of molybdenum, and if each cc of lead acetate solution is taken as equal to 0.016 gram of Molybdenum, then the calculation is made as follows. Suppose the ore gives 11.25% insoluble, then take $100 - 11.25$, or 88.75% as Molybdenite and $88.75 \times 0.6 = 53.25\%$ as Molybdenum, or 53.25 gram in the sample. Then the amount required is $53.25 - 0.01 = 53$ cc. Add 3 cc in excess, and continue boiling for ten minutes, when the precipitate should rapidly settle. When completely settled filter off through a 12½ cm fine paper, keeping the precipitate behind in the conical flask, and wash it six times by decantation with hot water. Then throw on the paper, and wash entirely from dissolved salt. Dry the ppt. completely, and ignite

without separating from the paper in a smooth porcelain or silica crucible. If the lead molybdate is properly washed and dried it will brush easily from the crucible, but if preferred, the crucible can be weighed before igniting. The ignition is performed first at gentle heat, then increased to a dull red, and continued so till the molybdate is a pale buff colour. The factor for Molybdenum is 0.2615, log 1.41260. The figure usually returned in the case of Molybdenite, however, is the percentage of MoS_2 , which is got by dividing the Molybdenum figure by 0.6, or direct from the PbMoO_4 figure by multiplying it by 0.4358.

Procedure B

In the case of siliceous ores carrying but little Molybdenum, 3–5 grams is taken to dryness in a 250 c.c. beaker flask with 10 c.c. pure HNO_3 , and a little (say 0.1 gram) KClO_3 . It is taken up with 20 c.c. dilute H_2SO_4 (4–1) and boiled to about half bulk. Dilute with water to 50 c.c., boil, allow to settle, filter through a 9 cm. or $12\frac{1}{2}$ cm. fine paper, and wash well with hot water into a 500 c.c. conical flask. Add dilute NH_4OH till a slight ppt. forms, clear with just enough dilute H_2SO_4 , bring the bulk up to 400 c.c. and pass a stream of H_2S into the solution for one hour. Shake the assay vigorously for two or three minutes, and allow to stand on a warm part for half an hour. When the ppt. is settled, and the solution clear, filter it off through a $12\frac{1}{2}$ cm. fine paper, and wash with hot H_2S water till free from iron, etc. Wash the ppt. back from the paper, add 20 c.c. of a 50% $(\text{NH}_4)_2\text{S}$ solution and allow to digest for ten

minutes on the hot plate Dilute to 40 c c., allow to settle, and filter through the same paper into a 300 c c conical flask, and wash with hot water with a 5% solution of $(\text{NH}_4)_2\text{S}$ till colourless solution comes through Render the filtrate just acid to litmus with dilute H_2SO_4 , pass H_2S again for twenty minutes, allow to settle on a warm part for twenty minutes Filter through a $12\frac{1}{2}$ cm fine paper, and wash with H_2S water once or twice Wash the ppt back into the flask, pour over the opened paper 10 c c pure HNO_3 , wash it in, and boil down till but 2 or 3 c c remain Dilute with water to 20 c c, add a slight excess of 1-1 NH_4HO , boil, allow to settle, and filter off through a 9 cm. fine paper into a 300 c c conical flask If there is no ppt, but merely fused sulphur, it is unnecessary to dissolve and reprecipitate If there is a ppt it is best to dissolve and reprecipitate Wash it back, dissolve in sufficient HNO_3 , bring to the boil, and reprecipitate the PbMoO_4 as in Procedure A, but in this case 5 grams of $\text{NH}_4\text{-Cl}$ and of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ will be enough

NICKEL

As with Cobalt, Nickel occurs as arsenide, Kupfernickel of sp. gr 7.3-7.7, hardness 5-5.5, streak brownish-black Another source is a silicate, Garnierite of sp. gr 2.4, hardness 3.4, streak greenish-white, and other silicates

Procedure A

The procedure for Nickel ores is the same as for Cobalt

ores The nickel remains in solution when Cobalt is precipitated as the double nitrite This solution is boiled in a 400 c c conical flask, and a slight excess of a strong solution of KOH added It is boiled again for five minutes, allowed to settle, and filtered off through a 12½ cm fine paper, the ppt being retained as far as possible in the flask, and washed six times by decantation with hot water. It is then washed on the paper till free from dissolved salts; dried, and ignited, and weighed as NiO Factor for NiO 7867, log of factor 1.89581

Procedure B

Should there be any residue suspected to contain Ni after acid treatment of the ore, it should be collected, dried, ignited, and fused in platinum with three times its weight of Na₂CO₃, dissolved out, acidified with pure HCl, taken to dryness taken up with pure HCl, boiled, diluted, filtered, and washed into the filtrate from the acid treatment, and Procedure A followed

PHOSPHORUS

Apatite is Phosphate of Lime Sp gr 3.1–3.2, hardness 5, and streak white Phosphorus occurs in very many rocks in small quantities

Procedure A

In very pure samples of Apatite weigh 0.5 gram into a 400 c c conical flask, add 10 c c pure HCl, and boil gently down to a syrupy consistency, add 5 c c of the

stock sodium acetate and Acetic Acid solution (see "Arsenic, Procedure A"), and 150 cc water. Bring to the boil, and titrate, boiling in the same way as in "Arsenic, Procedure A". The standard solution of Uranium Acetate is made by dissolving 35 grams in water with 25 cc $\text{CH}_3\text{CO}_2\text{H}$ and making up to a litre. Standardize it with pure $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$. Weigh up 2.3097 grams of the clearest crystals into a 400 cc. conical flask, dissolve in water, add 5 cc Sodium Acetate and Acetic Acid solution, make the bulk to the same as the above assay, and proceed as there described. The amount of Phosphorus in the standard is 0.2 gram, and should require 40 cc Uranium Acetate.

Procedure B

In complex ores and those containing but little P, which are decomposable by acids, take from 3–5 grams, place in a 250 cc beaker flask, acid take to dryness with 10 to 15 cc HNO_3 . Take up with 20 cc pure HCl, and boil for ten minutes. Dilute to about 40 cc and filter through 9 cm fine paper into a 400 cc conical flask, and wash well with hot water. Add 1–1 NH_4HO to the filtrate till a ppt begins to form, and just clear it with pure HCl. Through the hot solution pass a stream of H_2S to complete saturation. Bring the assay just to the boil, allow to settle, and filter through a $12\frac{1}{2}$ cm fine paper, and wash with hot water, acidified with 3 or 4 drops of pure HCl per 100 cc, and containing H_2S in solution. Boil the filtrate free from H_2S , oxidize with HNO_3 , till no further darkening occurs, add a cc or so in excess and boil again for five minutes. Precipitate the Fe, etc (which will carry down the P) as basic acetate as in "Iron, Procedure C".

It is reprecipitated with NH_4HO as there described, and washed. It is then washed into a 250 c c beaker flask, or, if too bulky, into a 400 c.c conical flask, sufficient HNO_3 is poured over the paper into the flask to dissolve the ppt (with the aid of heat), and the bulk reduced by boiling to some 60–70 c c. It is cooled to 85°F , and 30 c c of a solution of Ammonium Molybdate is added, the assay thoroughly shaken, and allowed to stand at about 85° for one hour. If a somewhat large excess of HNO_3 is present, it should be neutralized with 1–1 NH_4HO , and the solution just cleared with HNO_3 . The $(\text{NH}_4)_2\text{MoO}_4$ is prepared by dissolving 50 grams in 100 c c 1–1 NH_4HO . This solution is cooled, and poured slowly into 375 c c of 1–1 HNO_3 , shaking the mixture the while. This is cooled to room temperature, made up to 500 with water. It is allowed to stand overnight and is filtered before use.

The assay is filtered off through a 9 cm fine paper, and washed with warm water, adding 2 or 3 drops HNO_3 to each wash. Now transfer the funnel to a 400 c c conical flask, add 10 c c 1–1 NH_4HO to the vessel from which the assay is filtered, and pour on to the funnel. When this has sunk through, it is washed eight to ten times with hot water. Now neutralize with pure HCl and 5 c c in excess, add 5 grams NaCl , make the bulk to some 250 c c, bring to the boil, and add a strong solution of lead acetate till no further ppt forms, then 20 grams ammonium acetate. Boil for some ten minutes, allow to settle, filter through a 12½ cm fine paper, and wash thoroughly with hot water. Dry and ignite in a porcelain or silica crucible. Cool and weigh. The substance weighed is PbMoO_4 . To cal-

culate to equivalent of P, multiply the weight by 0 007 The factor for P_2 into P_2O_5 is 2 28866 Log of factor 0 35958

Procedure C

In the case of ones not decomposable by acids, the residue after usual treatment with acids is dried and ignited and fused with Na_2CO_3 , the silica removed as directed under "Silicon, Procedure C," and the estimation proceeded with as in Procedure B

POTASSIUM

There are many silicates of Potash, e g Orthoclase, sp gr 2 5, hardness 6-6 5, streak uncoloured Muscovite, sp gr 2 17-3, hardness 2-2 5, streak uncoloured The chloride occurs in Sylvine, sp gr 1 97, hardness 2, streak white, and in Carmalite

Procedure A

In the case of insoluble silicates, proceed by the "Lawrence-Smith" method, as described under Sodium The difference between the weight of the mixed chlorides and that of the NaCl found gives the weight of KCl Factor for KCl into K_2O is 0 6317 Log of factor 1 80051

SILICON

Silicon occurs abundantly as its oxide SiO_2 , Quartz of sp gr 2.65, hardness 7, and streak white, while the silicates of various metals also occur in great quantity

Procedure A

If it is desired to ascertain the purity of a good specimen of quartz, it may be evaporated with HF, and the residue weighed

Into a weighed small platinum capsule weigh 0.20 gram of the sample, which has been very finely agated. Add about 5 c c pure HF, and one drop of pure H_2SO_4 . Evaporate as dry as possible on a water-bath, then warm gently over a flame, and finally ignite, finishing for five minutes over the blowpipe. Repeat the HF and H_2SO_4 evaporation, and ignite again. Weigh. Add further HF and H_2SO_4 and continue till there is no more loss in weight. A blank evaporation of HF and H_2SO_4 is done, on the same quantities, and any residue allowed for in the assays. The loss in weight gives the amount of SiO_2 in 0.2 grams of sample.

Procedure B

Some silicates are decomposed by acid, and a gram of the agated sample may be weighed into a 250 c c beaker flask, and taken to dryness with 10 c c pure HNO_3 , and taken up with 20 c c pure HCl, and taken to dryness again, and thoroughly baked. Pure HCl is again added, say 10 c c, the assay brought to the boil for five minutes, and 40 c c hot water added, and the

assay again boiled, allowed to settle, filtered, and thoroughly washed. It is dried, and ignited before the blowpipe, in a weighed platinum or porcelain crucible, and weighed when cold as SiO_2 . Factor, if required for Si , 0.4702. Log $\bar{1}67228$.

Procedure C

In the case of silicates not decomposable by acids, 0.5 gram or 1 gram of the agated sample is treated with acid, if suspected to contain sulphides, and the residue filtered and washed, and ignited in a platinum crucible. It is then fused with four or five times its weight of about equal parts of Na_2CO_3 and K_2CO_3 . The heat is applied gently at first, and when all is molten, the heat is increased, and finally the blowpipe applied for ten minutes. The fusion is occasionally examined to see that all particles of the sample are included, and if necessary the mass is gently swung around to wash down any untouched particles. When fused, the melt is allowed to become quite cold, and is then placed in a 250 c.c. beaker flask, the crucible lying on its side, and just covered with water, and boiled out. The crucible is removed, and carefully washed in with hot water, and "policemanned" out. The solution is transferred to a 4 or 5-inch porcelain dish, the beaker carefully washed in and "policemanned," and pure HCl cautiously added till effervescence ceases, and then 5 c.c. in excess, and the assay evaporated to complete dryness, finishing in the oven till no suggestion of acid can be smelt. It is taken up with pure HCl till thoroughly moist, and again taken to complete dryness. Add 10 c.c. pure HCl , and bring to the boil, then 60-70 c.c. hot water, and boil again for five minutes. Allow

to settle, filter through a $12\frac{1}{2}$ cm fine paper, and wash three times by decantation with hot water, and finally on the paper till free from chlorides. Be careful finally to polish out the dish quite clean of any adhering particles of SiO_2 . Dry, and ignite strongly, in a weighed platinum or silica crucible, and when cold weigh as SiO_2 .

SILVER

An important source of Silver is Galena, which is never found entirely free from it. Native Silver is also common. Horn Silver is a natural chloride. Fahlerz also carries Silver.

The directions in the case of Gold ores generally apply to the assay of Silver ores. Where the ore is an ore of Silver (and not of Gold and Silver), the yield is generally so high as to favour the scorification assay. Take from 3 to 5 grams of ore, about 50 grams Pb, and Na_2CO_3 about 3 grams for a quartz ore, or borax 3 grams for a metallic gangue with the same of powdered glass for an ore with little or no SiO_2 . Mix the ore with half the Pb, spread the rest of the Pb on the top in the scorifier, and put the Na_2CO_3 or borax on top. When scorified, pour as in the gold assay. If the button of Pb weighs over 30 grams scorify it again. Then cupel. Silver is easily lost in cupellation by absorption in the cupel. The slag from the scorification is powdered, mixed with litharge, 20 grams, borax 5 grams, and two grams of

flour, run down in a crucible, and the button cupelled

The method of determining loss of Silver on cupellation is done by cupelling alongside the ore assays buttons of lead of the same weight, and containing the same amount of Silver. Antimony and copper will cause loss of Silver, loss is small in the case of Antimony and larger in the case of copper. A button of lead carrying appreciable Cu should be scorified again.

When assaying ores of Silver carrying a heavy percentage of Cu, a wet method of separating most of the Cu is often employed. Place 5 grams of the sample in a 400 c.c. beaker flask and add to it 30 c.c. of 1-1 pure HNO_3 . Allow to simmer on the water bath till no further brown fumes are evolved. Dilute with distilled water 300 c.c. and add pure HCl till no further precipitate forms, and a slight excess. Stir vigorously with a glass rod, and allow to settle completely (if necessary, overnight). Decant off through a medium fine $12\frac{1}{2}$ cm. paper, wash the precipitate and residue on to the paper, and wash once or twice, using a drop or two of pure HCl in the water. Dry thoroughly, brush off as much as possible from the paper and ignite the paper. Add the ash to the rest, and scorify. Ores carrying little Silver may, if suitable, be fused as Gold ores in the pot assay.

SODIUM

Common salt is the most common mineral of Sodium. Chili Saltpetre occurs abundantly, and there are many silicates of Sodium.

Procedure A

In doing an analysis of Salt, the moisture may be done on 10 or 20 grams in a platinum dish, being dried for an hour in the water oven. It may then be passed fairly rapidly over a Bunsen flame to raise the temperature somewhat above 100°C , but distinctly below redness. Cool in desiccator and weigh. The Sodium figure is got by difference, after estimating impurities.

The sandy insoluble matter is determined by dissolving 10 grams in 50 c c hot water with 5 c c pure HCl . Filter through a 9 cm fine paper into a graduated 50 c c flask, and wash well. Dry and ignite the paper, and weigh.

The lime is determined on the filtrate from the above which is made up to the mark in the cold. Take half = 5 grams. Add 10 c c. 1- NH_4HO , and 0.5 gram Ammonium Oxalate, and boil for twenty minutes. Filter through a 9 cm fine paper and wash well with hot water. Dry and ignite, and weigh as CaO .

Boil down the filtrate to some 200 c c., cool, add 5 c c 880 NH_4HO and 0.5 gram of Sodium Phosphate. Allow to stand overnight. Filter through a 9 cm fine paper, and wash with cold water containing 1-1 NH_4OH , and dry and ignite in porcelain or silica, and

blowpipe thoroughly to $\text{Mg}_2\text{P}_2\text{O}_7$. Calculate to MgO
Factor 3604 Log of factor $\bar{1}$ 55678

Determine the S in the other half of the 500 c c, by adding a saturated solution of Barium Chloride to the boiling solution till no more precipitate forms. Boil for twenty minutes. Allow to settle for an hour. Filter through a 9 cm fine paper, wash thoroughly with hot water, dry, ignite, and weigh as BaSO_4 . Factor for SO_3 0 3427 Log of factor $\bar{1}$ 53491

To estimate Chlorine dissolve 0.5 gram of the sample in about 100 c c of water in a porcelain basin, and titrate with a standard solution of AgNO_3 . The solution is thoroughly stirred during the slow addition of the standard solution. The indicator is 0.5 gram of K_2CrO_4 in 100 c c of water, and 10 c c is added before titration. The finish is indicated by a reddish flush persisting after vigorous stirring. The standard AgNO_3 solution is made by dissolving 23.94 grams in water and making up to a litre. Standardize this with pure KCl . Weigh up 0.5 gram, and dissolve and titrate as the assay was done. 0.5 gram KCl contains 0.2377 gram Cl . From this and the number of c c required, the standard may be calculated. The difference between the sum of the above determinations and 100, gives the percentage of sodium in the sample.

Procedure B

In dealing with Sodium minerals not soluble in water or acids, e.g. silicates, the "Lawrence Smith" process is used. It is as follows. Agate one gram of the sample, weigh it up, also one gram of pure NH_4Cl , and mix them intimately in a large agate mortar

Now weigh 6 grams of pure CaCO_3 , and mix with the sample and NH_4Cl in the agate mortar. Transfer the mixture to a piece of highly glazed clean white paper, rub around the mortar with two successive grams of pure CaCO_3 , and add to that on the paper. Now give the whole a mixing with a clean spatula, and transfer it to a platinum crucible. Tap it gently to settle the mass, and cover it with a platinum lid. Place over a small flame till no further NH_4Cl is evolved, increase the heat to good redness, and continue so for an hour. Allow to cool, dislodge the mass from the bottom of the crucible, and transfer it to a 250 c.c. beaker flask, wash out the crucible with hot water, and boil for ten minutes. Filter off through a $12\frac{1}{2}$ cm fine paper into a 300 c.c. conical flask, and wash well with hot water. To the filtrate add 2 grams pure $(\text{NH}_4)_2\text{CO}_3$, and boil for ten minutes, taking care the assay does not froth over. Add 2 c.c. 1- NH_4HO , and boil again for five minutes. Allow to settle and filter through a $12\frac{1}{2}$ cm fine paper into a 300 c.c. conical flask, and wash well with hot water. Boil down the filtrate to about 50-60 c.c. and transfer to a weighed platinum dish. Evaporate to dryness in a water bath, and dry for an hour in a water oven. Now cover with a clean clock-glass, and place over the smallest flame. If any decrepitating occurs, remove the heat, and replace in the oven for half an hour. Ignite again, and if no further decrepitating occurs, continue gently till no more dense fumes of HN_4Cl evolve, then, heat all over till incipient fusion. Cool, in a desiccator, and weigh quickly. The dish contains the sodium, and any potassium in the sample, both as chlorides. The chlorides are dissolved out of the dish

with water and the solution transferred to a porcelain dish, and thoroughly washed in. The bulk is made up to about 100 c c, and titrated as in Procedure A with AgNO_3 . From the weight of Cl found by titration its percentage in the mixed chlorides is found. The percentage of Cl in NaCl is 60.62, in KCl it is 47.54, so that the percentage found is either one of these figures, in the case of its being either pure NaCl, or pure KCl, or, if not, then somewhere between them, approaching the higher figure as the NaCl preponderates, and the lower one in the case of more KCl. Each per cent of Cl in excess of 47.54 represents 7.63% of NaCl in the mixed Chlorides. The factor for NaCl into Na is 0.3931, log of factor $\bar{1}.5944$. The result usually returned is "soda," Na_2O . The factor for NaCl into Na_2O is 0.5302, log of factor $\bar{1}.72444$.

STRONTIUM

Celestine is a sulphate of Strontium of sp. gr. 3.96, hardness 3-3.5, and streak white. Strontianite is a carbonate, sp. gr. 3.68, hardness 3.5-4, and streak white.

Procedure A

In the case of the sulphate, fuse 1 gram of the sample in a platinum crucible with 5 grams of a mixture of Na_2CO_3 and K_2CO_3 , and extract with hot water in a porcelain dish, neutralize with pure HCl, add 5 c c in excess, and take to dryness on the bath,

finish for half an hour in the oven. Take up with 10 c c pure HCl, bring to the boil, dilute to 50 c c. with hot water, boil again, allow to settle, filter off any SiO_2 through a 9 cm fine paper into a 300 c c conical flask, and wash well with hot water. Precipitate sulphides of metals of Group 2 with H_2S , filter and wash them. Remove Iron and Alumina as basic acetates as described under "Iron, Procedure C". Any Manganese is separated with Br from the filtrate as described in "Analysis of Wolfram". To the filtrate from Mn, if any, add 10 c c 1- NH_4OH , and excess of $(\text{NH}_4)_2\text{CO}_3$. Shake very thoroughly and allow to stand for two hours. Filter through a 12½ cm fine paper, and wash with cold water containing 1 c c NH_4OH per 10 c c of water. Wash back the ppt into a 250 c c beaker flask, dissolve in just enough pure HCl, add excess of 1- NH_4HO , acidify with $\text{CH}_3\text{CO}_2\text{H}$, and ppt any Ba with a 5% solution of $\text{K}_2\text{Cr}_2\text{O}_7$. Filter it off through a 9 cm fine paper, and wash with a 10% solution of Ammonium acetate into a 750 c c conical flask. Bring the bulk to some 500 c c. Make it just alkaline with 1- NH_4HO , add 50 grams pure $(\text{NH}_4)_2\text{SO}_4$, and boil down to two-thirds the bulk. Allow to settle, filter through a 12½ cm fine paper, wash with a 10% solution of $(\text{NH}_4)_2\text{SO}_4$. Wash finally five or six times with alcohol, dry, and ignite in the paper in a silica crucible, and weigh when cold as SrSO_4 . The factor for Sr is 0.4770. Log. of factor
I 67852

SULPHUR

The chief ore of Sulphur is Iron Pyrites, sp gr 4.9-5.1, hardness 6-6.5, streak greenish-black. It occurs native in volcanic districts in some quantity.

Procedure A

In the case of good samples of Pyrites 0.5 gram of the ore is treated in a 250 c.c. beaker flask with 20 c.c. of pure HNO_3 . This is added slowly, so that spontaneous action shall not be too violent. When it has ceased, the assay is allowed to digest slowly till no more brown fumes are seen. It is cooled, and about 0.1 gram pure KClO_3 added, and warmed again cautiously. When no more green fumes come off, it is slowly boiled down to a paste, cooled, and 20 c.c. pure HCl added, and two or three drops of Bromine. It is allowed to stand on a warm part for ten minutes, and then boiled down to half bulk. All should now be in solution but siliceous matter. If any globules of sulphur are observed, add more bromine, 10 c.c. pure HCl , and allow to stand again. Boil again to half bulk. Dilute with hot water to 100 c.c., add a slight excess of pure 1- NH_4HO , and boil for three minutes. Allow to settle, and filter through a $12\frac{1}{2}$ cm. fine paper into a 500 c.c. conical flask, and wash six times with hot water. Invert the funnel, and wash off the ppt. into the beaker flask, dissolve in just enough pure HCl , bring to the boil, add a slight excess of 1- NH_4HO , allow to settle, and filter through the original paper into the first filtrate. Wash six or

eight times. Render the filtrate acid to litmus, avoiding any but small excess, with pure HCl, bring to the boil, and add a hot saturated solution of BaCl_2 till no further ppt is formed. Boil carefully for thirty minutes, and allow to settle for an hour. Filter by decantation through a $12\frac{1}{2}$ cm fine paper, and wash three times by decantation with hot water. Get the ppt on the paper, and wash free from chlorides. Dry at 100°C , detach most of the ppt from the paper on to a clean clock-glass, ignite the paper in a silica or porcelain crucible, add the ppt, and ignite at a dull red heat till white. When cool, weigh as BaSO_4 . Factor for S=0.1373, log of factor $\bar{1}$ 13779.

Procedure B

In the case of insoluble minerals, e.g. Gypsum, Sulphate of Calcium, Barytes sulphate of Barium, etc., 0.5 gram of agated sample is fused in a platinum crucible with 3 grams pure Na_2CO_3 , gently at first and finally very strongly for thirty minutes. When cold it is boiled in a 250 c.c. beaker flask with water. The insoluble carbonates remain, and sodium sulphate goes into solution. Remove the crucible, wash it well with hot water, boil till the fused mass is broken up, and filter into a porcelain dish of some 300 c.c. capacity, and wash well with hot water. Acidify the filtrate with pure HCl, placing a clock-glass over the dish to prevent loss by effervescence, and add 10 c.c. in excess. Wash in the cover and evaporate to dryness on the water-bath till no pungent acid can be smelt. Add 10 c.c. pure HCl, bring to the boil, add about 60 or 70 c.c. hot water, boil for ten minutes, allow to settle, and filter off SiO_2 through a 9 cm. or

12½ cm fine paper into a 500 c c conical flask, and wash thoroughly with hot water. The filtrate is ready for precipitation as in Procedure A with Barium Chloride

Procedure C

In the case of ores carrying only about 10% take 1 gram, or those with less 2 grams, and take to dryness in a 250 c c beaker flask with about 0.1 gram pure KClO_3 , and 15 c c pure HNO_3 , take up with 20 c c pure HCl , and proceed as in Procedure A

THORIUM

Thorianite, an oxide, has a sp gr of 8-9, hardness 7. Thorite is a silicate of sp gr 4.5, hardness 4.5. Thorium is also found in Monazite sand, a phosphate of metals of the cerium group and thorium. Sp gr 4.5, hardness 5. The determination is done as follows. Fuse 0.5 gram or 1 gram of the fully agitated ore in 10 grams pure fused KHSO_4 for five minutes after first emission of fumes. Allow to cool, and dissolve out the fusion with hot water, and 10 c c pure HCl . Boil for ten minutes, having a bulk of some 50 c c. Allow to settle, filter and wash with hot water through a 9 cm fine paper. Bring the bulk to some 200 c c and add a slight excess of 1-1 NH_4HO , bring to the boil, allow to settle, filter through a 12.5 or 15 cm fine paper, and wash out sulphates. Wash back the ppt from the opened paper, pour over it 10 c c pure HCl , wash.

Bring the solution to the boil, and when all is in solution, dilute to 200 c.c. with cold water. Add 30 c.c. of a saturated solution of oxalic acid, cold. Shake thoroughly for five to ten minutes, and allow to stand overnight. Filter through a $12\frac{1}{2}$ cm fine paper, and wash with warm (60° C.) water. Get all the ppt. on the paper, dry and ignite. Fuse the oxides in 5 grams KHSO_4 , dissolve out in hot water and 10 c.c. pure HCl , boil till solution is complete, add slight excess $1\text{-NH}_4\text{HO}$, bring to the boil, allow to settle, filter and wash through a $12\frac{1}{2}$ cm fine paper free from sulphates. Wash back into 750 c.c. conical flask, add enough pure HCl to dissolve, but avoiding much excess, bring to the boil and add 4 grams pure ammonium oxalate. Shake vigorously for five to ten minutes, and allow to stand overnight. Filter through a $12\frac{1}{2}$ cm fine paper, wash with hot water containing 2 c.c. pure HNO_3 per 100 c.c. Wash back ppt into a porcelain basin with as little water as possible, and eight or ten times with hot strong HNO_3 . Evaporate to dryness on the water bath, allow to cool, add 10 c.c. pure HNO_3 (sp. gr. 1.4) and 20 c.c. fuming HNO_3 , and cover with clock-glass. Digest on the water-bath till action ceases and no brown fumes evolve. Wash in the clock-glass, rinse down the basin with a little hot water and evaporate to dryness, moisten again with water and bring again to dryness. Take up with 20 c.c. hot water, and transfer to a 250 c.c. beaker flask. Bring the bulk to 100 c.c., add 10 grams pure NH_4NO_3 , and warm up to 80° C., and add 20 c.c. 3% solution of H_2O_2 . Filter off through a $12\frac{1}{2}$ cm coarse paper, wash six times with a 2% solution of NH_4NO_3 . Wash back the ppt., dissolve in 1-HNO_3 , transfer to a basin,

evaporate to dryness, moisten with water, dry again, add 100 c c 10% NH_4NO_3 , and the Thorium again precipitated with H_2O_2 , filtered and washed again with a 2% solution of NH_4NO_3 , then dried and ignited and weighed, when cold, as ThO_2 . Factor for Th is 0.8790
Log of factor $\bar{1}$ 94399

TIN

Practically all the Tin of commerce occurs as Cassiterite, SnO_2 , sp gr 6.8–7.1, hardness 6–7, streak brownish to greyish.

Procedure A

In cases of pure or nearly pure samples of Cassiterite 0.3 gram of the fully agitated ore is fused in an iron or nickel crucible of 40 c c capacity with about 2 grams of Na_2O_2 . When the mass is molten, it is gently swung around to incorporate all the mineral, and maintained at a dull red heat for two minutes. The fusion is always carried out with a cover. Allow to cool, wash the lid into a 400 c c beaker flask. About 50 c c cold water is placed in the flask, and the assay carefully placed in it, and tilted over to allow the water to flow into the crucible. The beaker flask is next covered. When spontaneous reaction has ceased, the edge of the crucible remaining above water is washed, and the crucible raised to the mouth of the vessel with tongs, and carefully washed with hot water into the flask. The crucible is rinsed with 5 c c pure HCl , and washed

again into the vessel. Pure HCl is now added until the solution is clear, and any iron scale that is formed allowed to settle. The solution is decanted into a 750

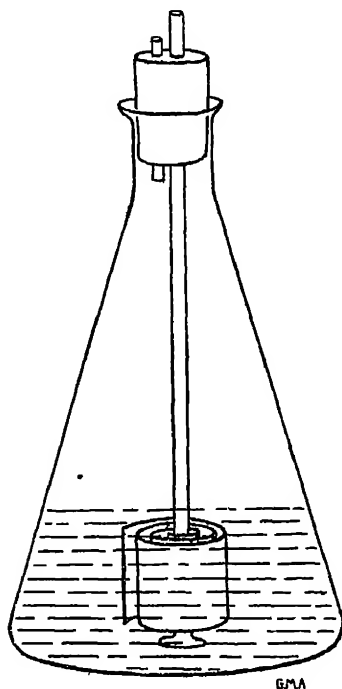
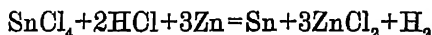


FIG 3

c c. round flat-bottomed flask through a funnel with a small packing of glass-wool which has been rinsed with dilute HCl , to retain the iron scale, if any. The glass-wool is thoroughly washed with hot water, and the bulk of liquid in the flask brought to some 400 c c. It

is cooled to about 80° F and 6 grams of Zinc dust gradually added; the assay being swung around at each addition. Iron is reduced, and the tin brought down as metal.

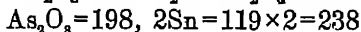
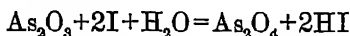


Now add gradually, shaking at each addition, 50 c.c. pure HCl. When the acid is all added, the assay is brought just to the boiling point, and a coil of nickel supported on a glass rod is lowered into it, which is held in place by a cork in the mouth of the flask. The cork is pierced with two holes, one to hold the glass rod, and the other to allow gas formed by reduction of the nickel to escape. The nickel coil should be some inch and a half in depth by four inches long, and coiled so that the liquid may have free circulation among the coils. (See Fig 3.) The assay is kept reducing thus just below boiling point for fifteen minutes. When it is removed from the heat a piece of *hard* white marble, the size of a large pea, is carefully introduced, the cork immediately replaced, and the assay placed in a stream of cold water till cold. The nickel is raised to the neck of the flask, it is washed in rapidly with about 5 c.c. cold boiled distilled water, then 5 c.c. freshly prepared starch solution is poured over it, the assay rapidly titrated with a standard solution of Iodine. The finish is indicated by a blue colour in the solution. The use of soft marble in this experiment is attended by the danger of too rapid disintegration, and possible frothing over of the assay. The layer of CO_2 formed on the top of the liquid prevents oxygen of the air from oxidizing the Stannous chloride. There should be a small residue of marble with slight evolution of gas at the end of the titration. The standard solution of

Iodine is prepared by placing in a litre flask 10.67 grams resublimed Iodine with 20 grams KI, covering with distilled water, and allowing to dissolve. When all the Iodine is in solution the bulk is made up with distilled water to a litre. The best means of standardizing this solution is with pure As_2O_3 . The reaction in the case of Tin in the titration is as follows.



In the case of Arsenic



Then 0.2 grams As_2O_3 correspond to 0.2404 grams Sn. To standardize weigh into a 400 c.c. conical flask 0.2 gram pure As_2O_3 , add 10 c.c. distilled water, and one gram pure stick NaOH. Boil gently till all is dissolved, make up the bulk with cold distilled water to 250 c.c., add a small piece of litmus paper, and render the solution just acid with pure dilute HCl. Then add 3 grams pure Na_2CO_3 , allow to dissolve and cool, and titrate with the standard Iodine. The test should take 48 c.c. Run in the Iodine to within a c.c. or two of the amount required, then add 2 c.c. starch solution, and finish to one drop. If correct, 1 c.c. standard Iodine solution equals 0.005 gram Tin.

Procedure B

Each sample of Tin ore should be duplicated by acid-cleaning before fusion. The 0.3 gram of sample is weighed into a small (say 100 c.c.) beaker, and treated with 5 c.c. pure HNO_3 , and allowed to simmer for ten minutes after disappearance of brown fumes. It is

then diluted with water to 15 c.c. and allowed to stand on a warm spot till settled. Filter through double 9 cm fine paper by decantation, adding 2 or 3 drops of acetic acid to the papers immediately before pouring off. When the liquid has sunk through, add 3 drops of acetic acid to the ore in the beaker, and very carefully wash it on the papers with hot water, washing also the papers gently around the top. Finally divided Tin oxide has a great tendency to go through papers, but the addition of acetic acid and the gentle use of the wash-bottle will result in perfectly clear filtrates. Two washes after the ore has all been policemaned out of the beaker, always with the use of acetic acid, washing each time gently around the top of the paper, will be sufficient. The ore is dried and ignited in the crucible in which it is to be fused, and the assay continued as in Procedure A. As some ores carry "soluble tin," sometimes to a considerable extent, it is necessary to examine the acid solution for it. Render alkaline with 1-NH₄HO, boil for a few minutes, allow to settle, filter and wash out nitrates. Wash back into the beaker, pour over the paper 5 c.c. pure HCl, wash it in, boil till clear, make the bulk up to about 70 or 80 c.c., bring nearly to the boil, and pass a stream of H₂S till saturated. Allow to settle, filter and wash. If the ppt. is a pale buff colour, it may be dried, and gently ignited with main part of the assay. If it is dark, showing the probable presence of copper, it must be treated with a 20% solution of K₂S by pouring about 10 c.c. over it, and washing till colourless. The tin is recovered from solution by adding a slight excess of pure HCl, and filtering and washing the sulphide free from chlorides. It is then

ignited with the main bulk, and the assay proceeded with as above

Procedure C

In the case of ores containing much siliceous insoluble matter, a good method is to give it a preliminary acid treatment, and then remove the bulk of the SiO_2 by evaporating with HF in platinum

A suitable quantity of the ore, determined by examination of the sample on the "pan," carrying not more than 0.3 gram of tin oxide, is weighed into a 20 c c Phillips beaker, and treated with 10 c c HNO_3 , and taken to dryness. It is taken up with 15 c c pure HCl, boiled gently for ten minutes, and diluted with water to 100 c c, allowed to settle, and filtered through double $12\frac{1}{2}$ cm fine papers, acetic acid being used as in Procedure B. The ore is all policemaned on to the paper, and washed gently till free from chlorides. The filtrate is examined for soluble tin as in Procedure B. It is then ignited in a platinum dish of some 30 or 40 c c capacity, and when cold the mass is covered with HF which is poured on it very slowly, one drop H_2SO_4 added. The dish is gently shaken to moisten the whole, and the dish placed on a warm spot to evaporate the HF without boiling or spitting. If much silica appears to remain unattacked, the HF treatment is repeated. When quite dry it is placed over a small Bunsen, and the heat gradually increased to a good red heat, and continued till no fumes are evolved. When cool, it is fused (being covered with a porcelain lid) with 5 grams of pure fused KHSO_4 . The fusion is conducted slowly till fumes of H_2SO_4 appear, and then at a dull red heat for two or three minutes. It is

allowed to cool thoroughly, the dish is nearly filled with hot water, when the fused mass will detach itself. It is transferred to a 250 c c beaker flask, policemaned in, and boiled (bulk about 100 c c) till the lumps of sulphate are dissolved. Excess of $1\text{-NH}_4\text{HO}$ is added, it is boiled again, allowed to settle, filtered and washed (use acetic acid and double paper). It is dried, ignited, and fused as in Procedure A.

Procedure D

In the case of ores, other than siliceous ones, e g in Wolfram, the tin is determined, when in small quantities (that is under one per cent) in the insoluble residue from the opening up of the ore "soluble tin" having been recovered, and added to it. It is fused in a small nickel crucible, the fusion dissolved out in hot water, rendered acid with pure HCl, transferred to a 300 c c conical flask, and 10 c c excess of acid added, the bulk is brought up to some 150 c c, a nickel coil inserted and the assay reduced for thirty minutes, after the yellow colour of ferric iron is gone. It is cooled and titrated as in Procedure A. When the tin occurs in greater quantities than 1%, the use of zinc dust is resorted to.

NOTE—It is essential that a test should be run on all materials used in this assay. Some iron crucibles, especially if there are traces of copper in their composition, will take an appreciable amount of iodine when subjected to a "blank" test, as also will some nickel ones. The "blank" is run on the same amounts of materials as are used in the actual assays, and should show a blue coloration with one drop of iodine, or at most two drops. It is best to reject

materials requiring more than two drops, but if no better are available, the "blank" must be very carefully determined, and subtracted from the cc required by the assay. The fusion in the "blank" test must be of equal duration as in the assays.

TITANIUM

Rutile, TiO_2 , with sp gr 4.12, hardness 6-6.5 and streak pale brown, and "Titaniferous iron" are the chief minerals of Titanium.

Procedure A

In the case of good samples of Titanium ores take 0.5 gram of the fairly agitated sample, and ignite in a silica or porcelain crucible for ten minutes; cool, and add 5 grams pure fused KHSO_4 in powder. Cover the crucible, and ignite gently till water is expelled, and increase the heat gradually to a bright red, taking care that the assay does not froth over. Remove from the heat, and while molten, rotate gently to include any specks of unfused ore on the sides, replace cover, and continue at a good heat for ten minutes. Allow to cool completely. Wash out with cold distilled water into a 250 cc beaker flask, and dissolve in the cold, and filter off through a 9 cm. fine paper into a 750 cc conical flask and wash with cold water and a few drops of dilute H_2SO_4 till nothing further dissolves. There will remain silica, and possibly sulphates of Ta and Nb. Add dilute NH_4HO to the solution till a ppt

forms, just clear it with dilute H_2SO_4 , bring the bulk to 500 c c with distilled water, add 50 c c of H_2SO_4 , and boil down to about 150 c c. The ppt of oxide of titanium is allowed to settle, and filtered off through a fine paper $12\frac{1}{2}$ cm. and washed with hot distilled water till free from sulphates. The ppt is dried and ignited to a pale buff colour in a porcelain or silica crucible, and weighed as TiO_2 . The filtrate should be diluted to 500 c c again with distilled water, 5 c c H_2SO_4 added and the solution again boiled down. If any more titanium oxide is formed, it is filtered and washed, and added to the first precipitation. Factor, if required for $\bar{I}=0.60$, $\log \bar{I} 77815$.

Procedure B

In the case of ores carrying little TiO_2 , one or two grams are finely agated, and brought to dryness in a 250 c c beaker flask with 10 c c pure HNO_3 . It is taken up with 20 c c pure HCl , boiled for five minutes, diluted to 50 c c and filtered through a 9 cm fine paper and washed with hot water. The residue is dried and ignited, and fused as in Procedure A with KHSO_4 . It is extracted with hot water with the help of 5-10 c c pure HCl , and the insoluble portion filtered off and washed with hot water. The solution is filtered into the original filtrate, from the acid treatment. Most of the acid is neutralized with dilute NH_4OH , and a stream of H_2S passed until saturated, any ppt is filtered off through a 9 cm or $12\frac{1}{2}$ cm fine paper, and washed with hot H_2S water. The filtrate is boiled free from H_2S , the Fe oxidized with HNO_3 , which is added till the solution no longer darkens, and boiled again for five minutes. The Ferric Iron is then precipitated as

basic acetate, as described in "Iron, Procedure C," bringing down also the Titanium. This ppt is dissolved and reprecipitated with NH_4OH , and washed three or four times. It is then washed back into a 750 c c conical flask, dissolved in sufficient dilute H_2SO_4 , and the Ti then estimated as in Procedure A.

TUNGSTEN

The minerals from which most of the Tungsten of commerce is obtained are Wolfram, which is Tungstate of Iron and Manganese in varying proportions, and Scheelite, Tungstate of Lime. Wolfram has a gravity of 7.2-7.5 and a hardness of 5.5, with a chocolate coloured streak, while Scheelite has a gravity of 5.9-6.1 and hardness of 4.5-5, with a white streak. Other minerals of Tungsten are Stolzite, Tungstate of Lead, and Hubnerite, Tungstate of Manganese.

Procedure A

In the case of high-grade Wolfram, and Scheelite ores, going from say 60% of Tungstic Acid (in which form the result of the assay is returned) to over 70%, one gram of the sample, which has been reduced to the utmost fineness in an agate mortar, is weighed into a dry 250 c c beaker flask. A word upon the agating of the sample. This should be done in parts of about half a gram at a time, and ground until there is no suggestion of scintillating specks in the motor, and the agated parts united and given a final

rub around Upon the proper agating of the sample depends the successful decomposing of Wolfiam Pour upon the ore boiling HCl of the strength of one part of pure acid to one of distilled water, to half the capacity of the vessel, cover with a watch-glass, or porcelain lid, and boil briskly, shaking the liquid around, especially at the beginning of the treatment, to prevent the Tungstic Acid which is forming from caking on the bottom of the vessel When the volume of liquid is reduced to about 15 c c remove from the heat and add 5 c c pure HNO_3 and 10 c c pure HCl, and boil gently down again to about 10 c c The Wolfiam should now be decomposed, and show a bright yellow colour, without any dark greenish particles on shaking the assay around Dilute the assay with hot distilled water, add 0.10 gram of Cinchonine, and allow to settle on a warm part till clear Filter through a 9 cm No 1F Munktel's or similar paper in a small funnel, pouring off the clear liquid, and getting as little as possible of the yellow-oxide on the paper Let the solution sink right through and wash carefully around the top of the paper with hot water Wash around the beaker flask with hot water to about 10 c c, let the assay settle, which it does rapidly, and pour off through the paper Wash this carefully by decantation twice, washing around the top of the paper each time Wash off any oxide that has got on the paper into the beaker flask with a small amount of hot distilled water, place the funnel in the beaker flask, and pour on to the paper 5 c c of $1-1\text{NH}_4\text{HO}$, let it run through, and rotate the assay till the yellow oxide is dissolved Bring it just to the boil, and put the funnel in a 200 c c conical flask Add to the assay

about 0.1 gram of $(\text{NH}_4)_2\text{CO}_3$ and when settled, filter. Allow to sink right through, add another pinch of $(\text{NH}_4)_2\text{CO}_3$, and wash paper and beaker, getting finally the whole of the insoluble residue on to the paper, and keeping the bulk of the solution as low as possible. Keep the insoluble residue, wash the neck of the funnel into the flask, place in it a small funnel without a stem and boil down to from 8 to 10 c c and transfer it to a weighed crucible (preferably platinum), washing out the flask carefully with a drop of ammonia in the wash water. Evaporate completely to dryness, and ignite, gently at first, then more strongly, finishing for ten minutes at a bright red heat. Allow to cool. No matter how well the ore may have been opened up, it will always be found that Tungstic Acid, often as much as 1% and sometimes more has been left in the insoluble residue. It is therefore submitted to the following treatment. Place in a 200 c c beaker, and add 10 c c of a 10% solution of NaHO , and boil slowly till concentrated without spitting. Dilute with distilled water to 100 c c, bring to the boil, allow to settle, filter and wash, add to the filtrate a drop of methyl orange solution, and render the assay just acid with pure HNO_3 , then add a slight excess of 1- NH_4HO , and boil down till the excess is removed. Filter off any ppt through a 9 cm fine paper, and wash thoroughly. Render the filtrate just pink with a drop of pure HNO_3 , and add a saturated solution of mercurous nitrate till no further precipitate forms. Then add *one* drop of 1- NH_4HO , collect precipitate together by vigorous shaking, allow to settle, filter and wash through a 9 cm fine paper with hot distilled water, to which a few drops of the mercurous nitrate

solution are added. When thoroughly washed, dry and ignite in a porcelain or silica crucible, gently at first, and finally at a bright red heat. When showing a bright yellow colour, allow to cool, and brush it into the main part of the assay in the platinum dish. Weigh off as Tungstic Acid WO_3 . This should be tested for traces of silica brought into solution by the hot NH_4HO by evaporating to dryness with 2 c c of pure HF and one drop of $1-4\text{H}_2\text{SO}_4$, and igniting and weighing again. This will, in some classes of ore, amount to as much as 0.1%, occasionally in some scheelites even more. Where platinum is not available, and porcelain is used, the silica may be determined by fusing the WO_3 out with 5 grams of pure KHSO_4 , leaching out with water, boiling till decomposed, adding a small excess of $1-1\text{NH}_4\text{HO}$, and boiling off the excess. The silica can be carefully collected on a small paper, washed, ignited, and weighed.

Procedure B for Wolfram

The principle of decomposing Wolfram with NaOH may be applied as follows. 1.25 grams of the agated sample are placed in a 250 c c beaker flask with 20 c c. of a 40% solution of NaHO , and digested on the hot plate till concentrated to a syrupy mass. It is cautiously diluted with pure water to 150 c c, 2 drops of formaldehyde added, brought to the boil, and allowed to settle. Filter through a $12\frac{1}{2}$ cm fine paper, pouring off the clear liquid, and wash four times by decantation, and six times on the paper with pure hot water. Add a drop of methyl orange to the solution, and render it just acid with HNO_3 , then alkaline with

ammonia, and boil down till the bulk is under 250 c c and all ammonia is dispelled, cool thoroughly Transfer to a graduated 250 c.c flask and wash in, making up to the mark Mix thoroughly, allow to settle, and filter off 200 c c through a $12\frac{1}{2}$ cm fine dry paper. Render faintly acid with a drop of HNO_3 , bring to the boil, and precipitate mercury tungstate with an excess of a saturated solution of mercurous nitrate, add *one* drop of $1\text{-NH}_4\text{HO}$, and shake thoroughly Allow to settle, filter through a $12\frac{1}{2}$ cm fine paper, washing six times by decantation with hot water containing a few drops of the mercurous nitrate solution, transfer the precipitate to the paper, and wash out all sodium salts thoroughly Dry the precipitate and ignite gently in the paper in a porcelain or silica crucible, finishing the ignition at a bright red heat, the resulting oxide should be a bright yellow colour, and easily brush out of the crucible when cold, and weighed It may be tested for silica in a weighed platinum dish with 2 c.c. of pure HF, and a drop of $1\text{-H}_2\text{SO}_4$ As $\frac{200}{250}$ or $\frac{4}{5}$ of the original 1 25 grams are ultimately worked on, the resulting WO_3 is from one gram

The two procedures above may be applied to ores carrying as much as fifty per cent. of cassiterite, tin oxide When employing the acid treatment method on ores rich in tin, it will be necessary to increase the amount of ammonium carbonate used in washing, to, say half or three-quarters of a gram, and to use a double paper, in order to obtain a brilliant filtrate In the case of Scheelite, or mixed Wolfram and Scheelite, use always Procedure A

When dealing with very small quantities of Wolfram,

use Procedure B, but use 5 grams of the sample fractionating to 4 grams. In the case of small quantities of Scheelite open up with acid, take the assay to dryness, then begin Procedure B.

In the case of ores carrying arsenic, it is necessary to subject them to preliminary roasting in a porcelain crucible till no more smell of garlic can be noticed or fumes coming off. It is then brushed into the beaker flask, and policemaned out.

URANIUM

The chief ore of Uranium is Pitchblende, an oxide of sp gr 9-9.7, hardness 5.5, and streak olive green to black. Carnotite is a Uranium vanadate, Samarskite is a Uranotantalite.

Procedure A

In the case of good samples of Pitchblende one or two grams, and in poorer samples from 3 to 5 grams weighed into a 250 c c beaker flask, and 15 c c pure HNO_3 , with a pinch of KClO_3 are added, and the assay boiled gently for twenty minutes. It is then diluted to about 50 c c and 1-1 NH_4HO carefully added till much of the acid is neutralized. Then small lumps of $(\text{NH}_4)_2\text{CO}_3$ are cautiously added till the assay is alkaline, and then some 5 grams in excess. The assay is allowed to simmer just at boiling point for ten minutes, allowed to settle, and filtered off into a 750 c c conical flask through a $12\frac{1}{2}$ cm, or, if there is a copious

ppt a 15 cm coarse paper. It is washed three times with hot water. The paper is opened and the ppt washed back into the beaker flask, and dissolved in just enough pure HNO_3 , and the paper well washed in. Bring the solution to the boil, and retreat with 1-1 NH_4HO and $(\text{NH}_4)_2\text{CO}_3$ as in the first case, boil, settle, filter and wash again into the first filtrate. Repeat the dissolving and reprecipitation, making three precipitations in all, give the final ppt three or four washes. Boil the filtrate, watching it carefully, as the evolution of NH_4HO and $(\text{NH}_4)_2\text{CO}_3$, may cause frothing. Continue the boiling until a precipitate is formed, caused by throwing down of Uranium by removal of $(\text{NH}_4)_2\text{CO}_3$. Add pure 1-1 HCl slowly until the solution clears, and boil again for five minutes to expel last traces of CO_2 . Now add 1-1 NH_4HO in excess, agitate thoroughly and allow to settle completely. Pour off the liquid from the ppt through a 12½ cm fine paper, taking care to keep the ppt. behind in the flask. If the solution is a deep blue, due to copper in solution, add about 200 c c *boiled* distilled water to the ppt in the flask, agitate, allow to settle, and decant off again through the same paper. Now place the funnel with paper in the flask containing the ppt, sprinkle over it about 0.1 gram $(\text{NH}_4)_2\text{CO}_3$ powder, and give it one wash around the top, then add to the assay in the flask sufficient of the carbonate to dissolve the ppt, warming up, and keeping the funnel in the flask. When dissolved, the assay is cooled completely, 30 c c of "magnesia mixture" added, the assay is thoroughly shaken for five minutes, and allowed to stand for an hour. Place the funnel in another 750 c c conical flask, moisten it

with cold water if dry, and filter off the assay, and wash with cold water, adding to each wash 5 drops of 1-1NH₄HO, and a pinch of (NH₄)₂CO₃. Some six or eight washes will suffice. Bring the bulk of the assay to some 300 c.c. and boil down until a ppt forms, add pure 1-1HCl till clear, boil again for five minutes, add excess of 1-1NH₄HO, allow to settle completely. Decant off through a 12½ cm. fine paper, getting very little or none of the ppt on the paper, and wash twice by decantation with *boiled* distilled water. Next, place the funnel with paper in a fresh 750 c.c. conical flask, dissolve the ppt in (NH₄)₂CO₃, and pass through it bubbles of H₂S till the solution no longer darkens. Place on a warm place to collect the ppt, and filter through the same funnel, and wash with hot water and (NH₄)₂CO₃. Bring the bulk to some 400 c.c., and boil till ppt forms, and add 1-1 pure HNO₃ till acid, and about 2 c.c. of bromine water to clear the solution of sulphur. Boil for ten minutes, add excess of 1-1NH₄HO. Allow to settle completely, pour off through a 12½ cm. fine paper, wash twice by decantation with *boiled* water, then wash on the ppt. This ppt is a very gelatinous one, and cannot be washed when on the paper. The large wash by decantation since the addition of "magnesia mixture," however, will free it from fixed salts. It is essential that the ammonia used for the precipitation of the Uranium be pure and free from CO₂. When the liquid has sunk right through, the ppt is dried, and ignited gently till the paper is charred, and then more strongly in a porcelain or silica crucible, and finally blowpipcd. Cool and weigh as U₃O₈.

Procedure B

In the case of Carnotite and other ores carrying Vanadium, Procedure A is followed as far as the treatment with "magnesia mixture," filtering and washing. To the solution of Uranium and Vanadium is added a 25% solution of lead acetate till no further ppt forms. Allow to stand on a warm part to collect the lead vanadate. Filter off through a 9 cm. fine paper, and wash with warm water and $(\text{NH}_4)_2\text{CO}_3$. Boil the filtrate till a ppt forms, then add 1-1H₂SO₄ in slight excess, and the excess of lead is brought down as sulphate. Allow to settle, filter and wash through a 12½ cm fine paper into a 750 c c conical flask, using cold water for washing. Boil the solution for ten minutes, carefully add an excess of 1-1NH₄HO, and proceed as in Procedure A, pouring off, washing by decantation, dissolving in $(\text{NH}_4)_2\text{CO}_3$, passing H₂S, and so on to the end.

VANADIUM

The principal minerals are Vanadinite, lead vanadate of sp gr 6.6-7.2, hardness 2.75-3, and streak white, Mottramite, a lead-copper vanadate of sp gr. 5.9, hardness 3, and streak yellow. Carnotite contains uranium and vanadium, and Patronite is a sulphide.

Procedure A

In samples which do not contain uranium place 1

gram of the ore in a 250 c c beaker flask, and take to dryness with 10 c c pure HNO_3 , take up with 20 c c of 3-1 H_2SO_4 , and boil down till fumes of H_2SO_4 evolve, and continue the fuming for ten minutes. Allow to cool gradually, dilute cautiously to 50 c c with water, and boil for five minutes, or until the residue is white PbSO_4 , with sandy insoluble matter. Allow to cool, and stand for half an hour to settle out most of the lead. Filter off through a 9 cm or $12\frac{1}{2}$ cm fine paper into a 400 c c conical flask, and wash with cold dilute H_2SO_4 (4-1), thoroughly. If the insoluble matter is suspected to contain undecomposed vanadium mineral, it should be separated from the PbSO_4 with Ammonium acetate, the residue dried, and ignited, and most of the siliceous matter evaporated with HF in platinum with a drop of H_2SO_4 , and the residue fused out with KHSO_4 . The fusion is boiled out with water and 10 c c dilute H_2SO_4 , and filtered into the original solution in the 400 c c conical flask. Nearly neutralize the solution with dilute $\text{NH}_4\text{-HO}$, and pass a stream of H_2S to saturation while hot. Allow to settle and filter off through a $12\frac{1}{2}$ cm fine paper into a 750 c c conical flask and wash with H_2S water, acidified, with a drop or two of H_2SO_4 . Boil down the solution to about 300 c c. Cool to about 85°F , and run in a decinormal solution of KMnO_4 from a burette till the solution is permanently pink. Now run in a decinormal solution of FeSO_4 till the pink colour is just discharged. Add a measured amount of the FeSO_4 till a drop gives a deep blue colour on the spotting plate with Potassium Ferricyanide. Now titrate the excess with $\frac{\text{N}}{10} \text{K}_2\text{Cr}_2\text{O}_7$. Titrate 50 c c of

the FeSO_4 with the $\frac{N}{10}\text{K}_2\text{Cr}_2\text{O}_7$. Get the equivalent in $\frac{N}{10}\text{K}_2\text{Cr}_2\text{O}_7$ of the amount of FeSO_4 added, subtract the excess $\text{K}_2\text{Cr}_2\text{O}_7$. The $\frac{N}{10}\text{K}_2\text{Cr}_2\text{O}_7$ can usually be made up, so as to be correct, and is a very stable solution. It should, however, be periodically checked, perhaps once or twice a week. 1.39 grams of pure $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ should require 50 cc (or 0.2799 gram pure Fe wire) as in "Iron, Procedure A." Each cc. of $\frac{N}{10}\text{K}_2\text{Cr}_2\text{O}_7$ is equal to 0.0051 gram of V, or 0.0091 gram of V_2O_5 .

Procedure B

In the case of ores containing Uranium, e.g. Carnotite, the Vanadium is estimated as follows. One gram of the ore is opened up as in Procedure A. When the insoluble and any PbSO_4 has been filtered off and the solution in the 400 cc flask has been treated with H_2S and filtered and washed, the solution, after boiling off H_2S , is treated to a cautious addition of Na_2O_2 till distinctly alkaline to litmus paper. It is then brought to the boil, allowed to settle, and filtered through a $12\frac{1}{2}$ cm fine paper into a 750 cc conical flask and washed three or four times with hot water. The ppt is washed back into the flask, dissolved in dilute H_2SO_4 , reprecipitated with Na_2O_2 , boiled and filtered into the first filtrate, and washed well with hot water. The solution is rendered acid with $\text{CH}_3\text{CO}_2\text{H}$, and a strong solution of lead acetate added until no further precipitate forms. The assay is

allowed to stand on a warm spot for ten minutes to collect the ppt of Lead Vanadate. Filter through a $12\frac{1}{2}$ cm fine paper into a 750 conical flask, and wash with hot water, adding to each wash a few drops of ammonium acetate solution, some six times. The ppt is washed off the paper into a 250 c c beaker flask, 20 c c of $3\text{-H}_2\text{SO}_4$ poured over the paper, and it is washed in thoroughly with hot water. The assay is brought to the boil, cooled, and filtered off through a $12\frac{1}{2}$ cm. fine paper into a 500 c c conical flask, and washed eight or ten times with cold water and two or three drops of $3\text{-H}_2\text{SO}_4$. The solution is now rendered just pink with $\frac{\text{N}}{10}\text{KMnO}_4$ as in Procedure A, and that procedure followed to the end.

ZINC

The chief source of Zinc is the mineral Blende, ZnS , of sp gr 3.9–4.1, hardness 3.5–4, and streak brownish-white. Other minerals are Calamine, a carbonate, and a silicate, Smithsonite.

Procedure A

In rich samples of ores of zinc weigh 1 gram into a 250 c c beaker flask, add cautiously 10 c c pure HNO_3 , and when spontaneous action has ceased, boil down to dryness. Take up with 5 c c pure HCl , and boil gently for three minutes. Add 20 c c hot distilled water, 5 grams of NH_4Cl , 5 c c bromine water, a

slight excess of dilute NH_4HO , and boil for five minutes. Allow to settle, and filter through a $12\frac{1}{2}$ cm fine paper into a 750 c c conical flask, wash six times with hot distilled water. Wash back the ppt into the beaker flask, pour over the paper 10 c c pure HCl , and boil till ppt is dissolved. Cool slightly, and add 5 c c bromine water, and excess of dilute NH_4HO , boil, settle, and filter into original filtrate, and wash some eight or ten times. Render the filtrate acid with pure HCl , and add 15 c c in excess. To remove copper in solution, a strip of lead foil is hung in the flask, and the assay kept just boiling for thirty minutes. The foil is removed and gently washed with warm distilled water. Bring the bulk of the assay to 200 c c and titrate hot with a standard solution of potassium ferrocyanide, using a solution of uranium acetate as indicator. Do not boil the assay once the titration has begun. It is a good plan to extract about 10–20 c c of the assay, and keep it hot in another vessel, and titrate boldly until the remaining solution is overdone, then wash in the extracted portion and continue the titration carefully.

The standard solution of ferrocyanide is made by dissolving 43.2 grams in distilled water and making up to a litre. It is standardized with pure freshly ignited ZnO , which contains 80.34% Zinc.

Procedure B

In cases of ores carrying much Mn and other impurities, take from 2 to 5 grams of the sample in a 250 c c beaker flask, take to dryness with 10–15 c c pure HNO_3 , take up with 10 c c pure HCl , boil for five minutes, dilute to 50 c c, and filter through a 9 cm

or $12\frac{1}{2}$ cm fine paper Wash well into a 300 c c conical flask Bring the filtrate to the boil, and pass a stream of H_2S till saturated Filter into a 500 c c conical flask and wash any ppt, using H_2S water for washing Boil the filtrate free from the smell of H_2S , add pure HNO_3 till the solution darkens no more, and boil again for ten minutes Precipitate the Iron, etc, as acetate as described under "Iron, Procedure C," dissolving in HCl , and reprecipitating with dilute NH_4HO , having previously added 3 or 4 c c Br to the first filtrate before filtering the ammoniacal solution into it To the filtrate add excess of NH_4HO , bring to the boil, and filter off the Mn through a fine $12\frac{1}{2}$ cm paper into a 750 c.c conical flask, and wash well with hot water Next pass a stream of H_2S through the ammoniacal solution till no more ppt forms, and the solution becomes yellowish Allow to come to the boil, remove from heat, and settle completely for an hour in an inclined position Filter through a fine $12\frac{1}{2}$ cm paper which has been washed once with a solution of $(\text{NH}_4)_2\text{S}$ Get the ppt on the paper, rinse out the flask once with warm $(\text{NH}_4)_2\text{S}$ water and pour it on Wash back the ppt into the 750 c c conical flask from the opened paper, and pour over it 15 c c pure HCl , and wash in well Boil down to about 10 c c, dilute to 200 c c, and titrate as in Procedure A

ZIRCONIUM

The chief mineral of Zr is Zircon, silicate of Zirconium, with sp gr 7.5, hardness 4.7, and streak grey. Others are Baddeleyite and Brazilite.

The method found to give most satisfactory results is as follows:

Agate very finely 0.5 gram of the sample, and fuse it strongly in a platinum crucible, with 5 grams pure Na_2CO_3 . Give it a very thorough fusion extending to thirty or forty minutes. Boil out the fusion when cold by placing the crucible in a 250 c.c. beaker flask with 50 c.c. boiling water. Thoroughly clean the crucible with a policeman, and wash in carefully. Boil for ten minutes, allow to settle, filter, and wash on a fine paper of $12\frac{1}{2}$ cm. Wash with hot water ten or twelve times. Get the whole of the residue containing Zirconium carbonate on the paper, dry and ignite it. Fuse it with 5 grams pure fused KHSO_4 for five to eight minutes after first emission of fumes in a porcelain crucible. Allow to cool, and dissolve out with hot dilute (1-4) H_2SO_4 in a 250 c.c. beaker flask. Transfer to a 400 c.c. conical flask. Add 1-1N H_4HO till ppt just persists, clear it with dilute H_2SO_4 , and add 5 grams $\text{Na}_2\text{S}_2\text{O}_3$. Boil for five minutes, allow to settle, filter and wash on a $12\frac{1}{2}$ cm fine paper. Get all the ppt on the paper, wash some eight or ten times with hot water, dry, and ignite in a porcelain crucible.

Fuse with 5 grams KHSO_4 for eight to ten minutes. Allow to cool and dissolve out as above with dilute H_2SO_4 . Transfer to a 500 c c conical flask. Nearly neutralize the solution with 1-1 NH_4HO , and add a saturated solution of ammonium oxalate until the precipitate which forms is redissolved in the warm solution (say 80° C). Now add about an equal bulk of boiling water, and then pure HCl until no more precipitate forms. Allow to stand overnight. The ppt contains Thoria, and the Zn remains in solution. Filter through a 9 cm fine paper, wash with warm water into a 750 c c conical flask. The solution is boiled down with 20 c c pure H_2SO_4 to copious fuming to destroy the oxalates. Allow to cool, and cautiously add 200 c c cold water. Add a slight excess of 1-1 NH_4HO , allow to settle and filter through a 12½ or 15 cm fine paper, and wash out sulphates with cold water. Wash the ppt back into the 750 c c flask, and pour enough HNO_3 over the opened paper to dissolve the ppt. Wash the paper well. Bring the bulk up to 100 c c or so with water, add $(\text{NH}_4)_2\text{CO}_3$ to it until the precipitate formed only just dissolves, and pour it very slowly (drop by drop) into a boiling solution of ammonium salicylate (10 grams in 50 c c water). Boil the assay till bulk is brought again to about 100 c c and allow to settle. Filter and wash through a 12½ cm fine paper with a 5% solution of ammonium salicylate until the ppt is pure white. Dry and ignite the ppt in a silica crucible, fuse it with 5 grams fine fused KHSO_4 . Dissolve the cold melt in hot 4-1 H_2SO_4 . Transfer to a 750 c c conical flask, bring to the boil, and add a slight excess of 1-1 NH_4HO . Boil for two minutes, allow to settle,

filter through a $12\frac{1}{2}$ cm fine paper, and wash with hot water till free from sulphates. Dry, and ignite to ZrO_2 . The factor for Zr is 0.7389. Log of factor \bar{T} 186859

WOLFRAM ANALYSIS

Example of the Complete Analysis of a Wolfram Ore.

The main part of the Analysis can be done on two grams, finely agated, and opened up as described under "Tungsten, Procedure A," with the difference that the assay is taken carefully to dryness on boiling down with the second lot of acid, and is then taken up with 10 c c pure HCl, boiled gently for a few minutes, the lid carefully washed in, and the assay diluted with hot distilled water to about 30 c c., and allowed to stand on the warm plate till settled. The cinchonine in this case is omitted. "Tungsten, Procedure A" is followed, the assay being filtered into a 300 c c conical flask through a 9 cm fine paper, and washed by decantation as there described, dissolved in 1-NH₄HO, and so on to the end. The residue from treatment with caustic soda, together with any ppt brought down with NH₄HO from the soda solution are washed from the papers into a 200 c c beaker and taken to dryness with 5 c c pure HCl, then taken up with 5 c c pure HCl, diluted as

about 15 c.c., filtered through a 9 cm fine paper into the original filtrate from the two grams of ore. The residue is collected on the paper and washed, then dried and ignited in a small platinum vessel. When cold it is weighed, and treated with about 5 c.c. pure HF, and one drop 1-NH₂SO₄ carefully evaporated, and ignited strongly. It is treated again with HF and H₂SO₄, cooled, and finally weighed. The difference in weight represents the SiO₂. There will remain SnO₂, together with some of the Titanium, if present, and possibly some rarer metals as Tantalum and Niobium. It is fused out of the platinum with a gram or two of pure KHSO₄, when cold leached out with a small quantity of hot distilled water, and boiled down with an equal amount of pure HCl, allowed to settle, and filtered through a 9 cm fine paper into the original filtrate from which the tungstic acid was filtered. The final residue is washed, dried, ignited. We will refer to this as "residue A."

The filtrate, from which the WO₃, SiO₂, and most of the SnO₂, together with possible sulphates of Tantalum and Niobium have been removed, is partly neutralized with a 20% solution of NaOH, the bulk brought to about 200 ccm., and boiled. Into the hot solution a rapid stream of H₂S is passed to saturation, this brings down Cu, Bi, Pb, As, Sb, and any Sn brought into solution. It is again brought just to the boil, allowed to settle, filtered and washed thoroughly with hot water containing H₂S in solution. The filtrate will be referred to as "filtrate A." If the ppt with H₂S is a small one, as is generally the case in Wolfram ores, it is treated on the paper with a 20% solution of K₂S, filtered with a fresh vessel (say a 250 c.c. conical

flask) and washed till colourless. The filtrate contains As, Sb, and Sn. Call it "filtrate B." The ppt containing Cu, Bi, and Pb is washed into the vessel from which it was filtered, treated with 5-10 c c pure HNO_3 , and taken to dryness, then taken up with 10 c c of 3-1 H_2SO_4 , and boiled down till fumes are fully evolved. When cool, it is diluted to 15 c c with distilled water, and allowed to settle while the examination of filtrates A and B is proceeded with. To filtrate B add slowly a slight excess of pure HCl , warm up to about 90°C , and shake vigorously. The solution should smell strongly of H_2S , if it does not a further stream should be passed through it. Any precipitated As, Sb, and Sn sulphides are filtered and washed with hot H_2S water till free from chlorides, then dried, and ignited in a silica or porcelain crucible at first gently, and finally at a strong red heat. The SnO_2 remaining after ignition is added to residue A. This is then weighed, the tin is estimated as in "Tin, Procedure D," calculated to SnO_2 , and the weight of SnO_2 subtracted from that of residue A. This difference may be returned as Tantalum and Niobium. If there is an appreciable quantity of these metals (which is not often the case in Wolfram ores), they should be removed from the solution with the Tin after the titration. The Tin is just separated as Sulphide with H_2S , the H_2S boiled from the filtrate, and Ta and Ni precipitated with NH_4OH , filtered, washed, dried, and ignited, and returned as Ta_2O_5 and Nb_2O_5 . Filtrate A is boiled down till all the H_2S is expelled, 5 c c pure HNO_3 are added, and again boiled for three minutes. The Iron, Alumina, and Titanium are precipitated as basic acetates as

described under "Iron, Procedure C," the acetates are dissolved in pure HCl, reprecipitated with 1-1NH₄HO, filtered, washed, dried, and ignited. They are weighed as Fe₂O₃, Al₂O₃, TiO₂. After weighing the mixed oxides are mixed thoroughly by crushing in an agate mortar, and aliquot parts (say a half each) are weighed off. One part is treated in a 300 conical flask with 15-20 c c pure HCl, and the Iron determined as described under "Iron, Procedure A." The other portion is fused in a porcelain or silica crucible with five times its weight of KHSO₄, and the Titanium estimated as described under "Titanium, Procedure A." The total amount of Iron is calculated to Fe₂O₃ (factor 0.7), the total amount of TiO₂ is found, and these combined totals in the mixed oxides subtracted from the weight of those oxides gives the weight of Al₂O₃. The manganese is recovered from the filtrate from the "mixed oxides" as described under "Manganese, Procedure A." The filtrate from the manganese is reduced in bulk to some 350-400 c c, a few drops of 1-1NH₄HO are added, and H₂S passed into it. Zinc and Ni and Co will come down here. It is rare that Zn is found in Wolfram. If it is, it should be estimated on a separate portion of 3-5 grams of the 90 mesh sample by the method described under "Zinc, Procedure A." Traces of Co and Ni are sometimes found. These appear as black sulphides, and are filtered off through a 9 cm fine paper, thoroughly washed with hot water and (NH₄)₂S, dried, ignited and weighed, and returned as NiO and CoO. To the filtrate from Ni and Co, add about 0.5 gram ammonium oxalate, and boil for ten minutes. The

lime is precipitated and filtered off, and well washed and ignited very strongly in platinum. The filtrate from the lime is boiled right down until salts begin to separate out, pure HNO_3 is then added cautiously, and the assay again boiled down to a small bulk. It is cooled, and enough water added to keep all salts in solution in the cold. Then add about 0.5 gram of sodium phosphate in solution, and finally 10 c.c. NH_4HO , sp gr 880. The whole is thoroughly cooled and vigorously shaken, and allowed to stand in a cold place for some time, best overnight. It is then filtered off through a 9 cm or $12\frac{1}{2}$ cm. paper, and magnesia estimated as described under "Magnesia, Procedure A."

Arsenic on 3-5 grams as in "Arsenic, Procedure B." The amount of Phosphorus in a Wolfram does not often exceed a figure in the second place of decimals, and will count in the above analysis as Al_2O_3 . In strict accuracy, therefore, its amount, calculated to P_2O_5 , should be deducted from that figure. It is estimated as follows. Two grams of the sample are opened up as in the main analysis, being taken to dryness on the second addition of acid, then it is boiled with 5-8 c.c. pure HNO_3 till brown fumes are no longer evolved, diluted with an equal quantity of hot water, and allowed to settle. It is then filtered off by decantation through a double 9 cm fine paper into a 300 c.c. conical flask, and washed by decantation with a hot 5% solution of HNO_3 . This treatment brings all the Phosphorus into the filtrate. The bulk of the filtrate is reduced by boiling to some 50 c.c., a slight ppt is produced with 1-1 NH_4HO , 5 c.c. pure HNO_3 added, warmed till clear, and the

phosphorus estimated as described under "Phosphorus, Procedure B"

Sulphur is estimated on 3-5 grams. It is treated in a 250 c.c. beaker flask with 10 c.c. pure HNO_3 , and about 0.2 gram KClO_3 , and stood on the warm plate, brought slowly to dryness without baking. If any globules of sulphur are unoxidized, retreat with HNO_3 and KClO_3 . When all is oxidized take up the dried assay with 20 c.c. pure HCl , and boil till about a third of the bulk is evaporated. Then dilute to about 80 c.c. with hot distilled water, and allow thoroughly to settle till clear. Filter, and wash by decantation with hot water containing a few drops of pure HCl . Bring the filtrate to boiling point, neutralize most of the acid with 1-1 NH_4HO , and add an excess of a boiling saturated solution of BaCl_2 . Boil for fifteen minutes, and allow to settle overnight. Filter through a 9 or 12½ cm. fine paper, and wash thoroughly with hot water containing a few drops of pure HCl , and finally with pure water. Dry, and ignite strongly. Weigh as BaSO_4 . Factor for S is 0.1373. The part containing the Cu, Pb, and Bi is filtered, if any ppt. of Pb has formed, through a 9 cm. fine paper into a 250 c.c. beaker, and washed with a 1-4 solution of H_2SO_4 . The funnel is then placed in another vessel, and the lead sulphate estimated as described under "Lead, Procedure A."

The filtrate is carefully neutralized with NH_4HO , and a slight excess added, and Bi estimated as described under "Bismuth, Procedure B." The Cu remains in solution. If in considerable quantity, the solution is rendered just acid with pure HCl , and the Cu precipitated again as sulphide, and estimated as in

“ Cu, Procedure A ” If small, it is done colorimetrically as described in “ Cu, Procedure E ” Sb is estimated on 5 grams as described in “ Antimony, Procedure B.”

An assay for WO_3 should be done as in “ Tungsten, Procedure A.”



PART III

ON SOLUTIONS

(A) STANDARD SOLUTIONS

ANTIMONY titrations. 2.82 grams pure potassium biomate dissolved in distilled water, and made up to a litre

ARSENIC titrations 34 grams pure uranium acetate in powder form dissolved in distilled water, with 20 c c acetic acid added, and made up to a litre.
6.7732 grams resublimed iodine in 20 c c distilled water and 10 grams pure potassium iodide When quite dissolved made up to a litre

CHROMIUM titrations $\frac{N}{10}$ ferrous sulphate=27.8 grams in water, made up to a litre $\frac{N}{10}$ potassium bichromate=4.903 grams in water made up to a litre.

COPPER titrations 39.18 grams pure sodium hyposulphite in distilled water and made up to a litre

42 grams pure potassium cyanide in water and make up to a litre For colorimetric copper solution, 0.5 gram electrolytic copper in just

enough nitric acid, and, after boiling, make up to a litre with distilled water

IRON titrations 4.39 grams pure potassium bichromate in water, and make up to a litre
 2.82 grams pure potassium permanganate in distilled water and made up to a litre
 For colorimetric iron solution, dissolve 0.1 gram pure iron wire in just enough pure hydrochloric acid, add pure nitric acid, till oxidized, take to dryness, take up with 10 c.c. pure hydrochloric acid, and make up to a litre.

MANGANESE titrations. Potassium bichromate solution as in "Iron" titrations

TIN titrations 10.67 grams resublimed iodine in 20 c.c. water with 20 grams pure potassium iodide
 Rotate till dissolved, and make up to a litre

VANADIUM titrations. $\frac{N}{10}$ potassium permanganate = 3.1606 grams in water and make up to a litre
 $\frac{N}{10}$ potassium bichromate and $\frac{N}{10}$ ferrous sulphate as in "Chromium" titrations.

ZINC titrations. 43.2 grams potassium ferrocyanide in water, and made up to a litre

(B) INDICATOR SOLUTIONS

METHYL ORANGE (sodium salt of dimethylamide azobenzene-sulphonic acid) = 1 gram per litre of water.

POTASSIUM FERRICYANIDE 0.1 gram per 100 c.c. of water (make fresh each day)

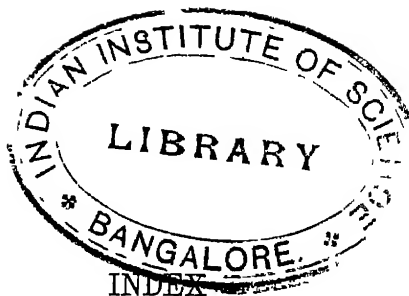
POTASSIUM FERROCYANIDE 10 grams in 100 c.c. water

STARCH SOLUTION Mix 1 gram with water, and pour into 200 c.c. boiling water, and boil for two minutes. Use cold.

URANIUM ACETATE. 0.2 gram in 100 c.c. water,



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